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FINAL REPORT

IMPROVED CHEMICAL METHODS FOR SAMPLING AND ANALYSIS OF GASEOUS POLLUTANTS FROM THE COMBUSTION OF FOSSIL FUELS

VOLUME II
NITROGEN OXIDES

Contract No. CPA 22-69-95

JULY 1971

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State-of-the-art manual methods are reviewed for the determination of oxides of nitrogen in stationary fossil fuel combustion sources for the concentration range 5-2000 ppm for nitric oxide (NO), nitrogen dioxide (NO_2), and total oxides of nitrogen (NO + NO_2 or NO_x).

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by
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and
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Prepared for
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Cincinnati, Ohio

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FOREWORD

The compilation of information contained in this publication was performed pursuant to Contract No. CPA 22-69-95, Air Pollution Control Office, Environmental Protection Agency.

The information was compiled by Walden Research Corporation and their subcontractor, Arthur D. Little, during the period June 12, 1969 to September 11, 1970.

Volume I of this report examines state-of-the-art manual methods for sampling and analysis of sulfur oxides. The determination of sulfur dioxide (10-3000 ppm) and sulfur trioxide (5-300 ppm) is reviewed for stationary fossil fuel combustion sources and for control equipment which may be installed to reduce the emissions from such sources.

Volume II reviews methods for the determination of oxides of nitrogen in stationary fossil fuel combustion sources for the concentration range 5-2000 ppm for nitric oxide (NO), nitrogen dioxide (NO_2), and total oxides of nitrogen ($NO + NO_2$ or NO_x).

Volume III of this report examines state-of-the-art manual methods for sampling and analysis of carbon monoxide in stationary fossil fuel combustion sources for the concentration range 10-1000 ppm.

The major pollutants of interest in this study are sulfur and nitrogen oxides. The report subsequently includes a literature search, review of methodology and laboratory investigation on the most promising methods. Carbon monoxide, the minor pollutant, was limited to a literature search and review of methodology.

This report has been reviewed and approved.

Robert L. Larkin

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Project Officer
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Environmental Protection Agency

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1. INTRODUCTION

This is Volume II of three volumes of the Final Report on "Improved Chemical Methods for Sampling and Analysis of Gaseous Pollutants from the Combustion of Fossil Fuels (in Stationary Sources)." The three volumes are divided by subject as follows:

I Sulfur Oxides
II Nitrogen Oxides
III Carbon Monoxide

This report was prepared under Contract No. CPA 22-69-95 covering the period June 12, 1969 to September 11, 1970. The principal objectives of this program were: (1) to review the state-of-the-art for manual (wet chemical) methods for the determination of emissions of specified gaseous pollutants from (indirect-fired) stationary fossil fuel sources, (2) to select and develop improved procedures for high precision emissions determinations, and (3) to select and develop simplified procedures where high precision determinations were judged to be complex (i.e., required a highly trained research and development group).

The determination of the oxides of nitrogen, significant in fossil fuel stationary combustion, is reviewed for the concentration range 5-2000 ppm for nitric oxide (NO), nitrogen dioxide (NO_2), and "total oxides of nitrogen" ($NO + NO_2 \equiv NO_x$). We have shown, on the basis of equilibrium calculations, that N_2O and HNO_3 (g) may be present at significant concentrations at low (i.e., near ambient) temperatures. For normal residence times, the slow kinetics of NO_2 formation suggest that HNO_3 will not be a significant product. Kinetic paths for the low temperature formation of N_2O have not been described quantitatively but are believed to be of minor importance. Where low temperature residence times become long as a result of the application of control techniques, these species may become of importance.*

---

*We do not consider methods of analysis for N_2O here. HNO_3 (g) would be found as NO_x in the usual phenol disulfonic acid (PDS) analysis. See Sections 3, 4, and 7 for further discussions and recommendations.

Since the practical utility of an analytical method is limited by the fundamental problem of obtaining a representative sample, we have necessarily discussed the principles of flue sampling and the limitations so introduced to the overall accuracy and precision of a given determination. General principles of flue gas sampling have been discussed in Volume I of this report. However, problems specific to sampling for the nitrogen oxides are included. The combustion effluent environment is treated in similar fashion.

In the following subsections, we consider method development priorities based upon national NO_x emissions and summarize the state-of-the-art in manual determination of NO_x in combustion effluents.

1.1 National NO_x Emissions and Method Application Priorities

A rough guide to method development priorities may be obtained from the relative contributions of various sources to national NO_x emissions (Table 1-1).

TABLE 1-1

NATIONWIDE EMISSIONS OF NO_x, 1966 (521)[†]

		10^6 tons/year
Total from fossil fuel combustion in stationary sources		6.5
By fuel	Coal	4.0
	Fuel oil	0.9
	Natural gas	1.6
By sector[*]	Power plants	3.5
	Industrial combustion	2.1
	Commercial and residential	0.9

[†] Literature references are listed at the end of the report.

[*] The "sector" figures given by NAPCA include 0.2×10^6 tons/year generated by combustion of wood. Arbitrarily subtracting these emissions evenly from the industrial and commercial and residential sectors yields the values given in Table 1-1.

In contrast to sulfur emissions, NO_x emissions are primarily equipment, rather than fuel, dependent (518). (However, both fuel heat content and organic nitrogen content are among the factors determining NO_x concentrations in the effluent.)

The categories above do not exclude fossil fuel effluents mixed with process emissions. A detailed breakdown, which excludes (direct-fired) process emissions, is available from work conducted at Walden (480) and is summarized in Table 1-2. As may be seen from the boiler category, 92% of total non-process emissions are attributable to watertube boilers, for which the smallest size range is about 25,000 pounds of steam per hour (ca. 3×10^7 Btu/hr). The NO_x emission problem (as is also true for SO_x) is, therefore, centered upon these relatively large sources which require the highest priority for NO_x method development. Unlike SO_x, gas-fired equipment is, here, a significant fuel.

TABLE 1-2

NATIONWIDE EMISSIONS OF NO_x, 1967
(excluding process emissions)*

		10^6 tons
Total		5.03
By fuel	Coal	3.47
	Residual fuel oil	.59
	Distillate fuel oil	.23
	Gas	.74
By sector	Utilities	3.42
	Industrial	1.03
	Commercial	.34
	Residential	.24
By boiler category (excluding residential)		
	Watertube > 500,000 pph	2.85
	Watertube $\leq$ 500,000 pph	1.55
	Firetube	.24
	Cast iron	.15

---

*Also excludes stationary internal combustion engines

It does not appear desirable to develop specially adapted high precision methods applicable to the numerous but relatively unimportant small sources of NO_x at this time.

1.2 Synopsis of Present State-of-the-Art in Determination of NO_x in Combustion Effluents

Almost all reliable determinations of oxides of nitrogen in combustion effluents have been made for total oxides ($NO + NO_2$) by the phenol disulfonic acid method. There are no reliable manual wet chemical analyses available for the NO_2 concentration in a combustion effluent so far as we have been able to determine. This situation has arisen as a result of the widely held, and correct belief that NO is by far the most important species generated in combustion, and the absence of convenient and accurate analytical methods for the individual oxides.

In the following section we summarize the effluent compositions from fossil fuel-fired stationary combustion sources. The emphasis is upon those factors which influence the selection of sampling and analytical methods for nitrogen oxides.

2. THE COMBUSTION EFFLUENT ENVIRONMENT

2.1 Introduction

A prerequisite for the selection of manual chemical methods for sampling and analysis of gaseous pollutants from the combustion of fossil fuels is the description of the environments to be sampled. The combustion products from all stationary sources such as steam generators, process heaters, water heaters, and air (space) heaters are to be considered, except for those cases where process emissions are combined with the combustion products, e.g., a lime kiln or blast furnace. The measurements will normally be required at stack conditions; however, they may also include conditions at the inlet and outlet of control equipment.

The combustion effluent environment has been described in some detail in Volume I of this report (Section 2 and Appendix 1). For convenience, we, here, briefly present the major conclusions from the previous discussion and include further detail relevant to NO_x determination.

For this evaluation, we have divided combustion equipment into three arbitrary size groups as shown in Table 2-1 in several approximately equivalent ways. There are relatively few suppliers of equipment in the large size range (four major sources) with 1968 annual sales of the order of 75 units (556). On the other hand, there are several hundred suppliers of small units with 1967 annual shipments of approximately 1,500,000 units (557). Useful life is perhaps 15 and 30 years, respectively, for the small and large units. Combining the large number of installed units with the disparate designs, range of fuels used, load factors, varying operating practices, etc., it is clear that it is totally impractical to attempt to specify the environment for individual cases. Rather, we have reviewed the range of environments reported in the literature for each of the three size categories shown in Table 2-1 for oil, coal, and gas. A summary of emission parameters is given in Table 2-2 in consistent units ($lb/10^6$ Btu). From these data the various requirements for principal factors such as required sensitivity, possible interferences, transients and temperature regimes may be determined.

TABLE 2-1

SIZE CATEGORIES FOR STATIONARY COMBUSTION SOURCES

	Large	Intermediate	Small
Btu per hour	$\geq 5 \times 10^8$	3×10^5-5×10^8	$< 3 \times 10^5$
Boiler horsepower	$\geq$ 15,000	10-15,000	$<$10
Pounds of steam per hour	$\geq$ 500,000	350-500,000	$<$330
Megawatts	$\geq$ 50	$<$50 MW	Not Applicable

2.2 NO_x Emission Concentrations

The primary variable affecting the choice of analytical methodology is the concentration of the species sought. As may be seen from Table 2-2, based upon average emission factors, NO_x concentrations will vary over an order of magnitude from small oil-fired equipment to large coal-fired boilers. Greater variation is clearly to be expected over the complete range of individual combustion equipment. The range of individual concentrations observed for industrial equipment is shown in Table 2-3 (93). The extreme range of NO_x concentrations are observed in large equipment. A comparison of the effect of fuel type on NO_x emission concentration has been given by Barnhart and Diehl (464) (Figure 2-1).

Cuffe and Gerstle (431) have determined the effect of equipment type and load on NO_x emissions for coal-fired equipment (Figure 2-2). The very high emission rate of the cyclone furnace and the high sensitivity of NO_x concentration to load condition for this unit are striking.

2.3 Control Technology

In contrast to SO_x control technology, NO_x control may best be achieved at present, at least in part, by control of combustion conditions. For gas- and oil-fired equipment the two-stage combustion

TABLE 2-2

EMISSION PARAMETERS FOR FOSSIL FUEL COMBUSTION[a] (pounds/10^6 BTU)

	GAS[b]			OIL[c]			COAL[d]		
	Large	Intermed.	Small	Large (Resid.)	Intermed. (Resid./Dist.)	Small (Dist.)	Large	Intermed.	Small
Velocity ft/min	2000-3000			2000-3000-			2000-3000		
Moisture	----- 18% @ 0% XS Air 15% @ 20% XS Air ------			----- 10% @ 0% XS Air 9% @ 20% XS Air ------			----- 6% (Nominal) ------		
Excess Air %	15	15-75	75	20	20-75	75	25	25-75	75-100
Stack Temp. °F (of Breeching)	275-400	400-750	750-900	300-400	400-750	750-900	300-400	400-750	750-900
CO	Neg.	$4x10^{-4}$	$4x10^{-4}$	$3x10^{-4}$	0.01/0.01	.01	0.02	0.1-2	2
SO_2	$4x10^{-4}$	$4x10^{-4}$	$4x10^{-4}$	1.65	1.65/0.31	0.31	3.5	3.5	3.5
SO_3				0.03	$0.016/3x10^{-3}$	$3x10^{-3}$			
NO NO_2	0.35	0.2	0.1	0.68	0.47/0.51	.08	0.8	0.8-0.3	0.3
Particulate	0.014	0.016	0.017	0.07	0.15/0.10	0.06	0.46 (90% cont.)	0.53 (65% cont.)	0.8 (uncont.)
Hydrocarbons	Neg.	Neg.	Neg.	0.022	0.01/0.01	.02	$8x10^{-3}$	0.04-0.4	0.4
Transients	10% of Capacity Per Min.			10% of Capacity Per Min.			5% of Capacity Per Min.		

a. Details in Appendix 1, Final Report, Vol. I

b. 1100 BTU/SCF

c. $S_{dist.}$ 0.39%, 142,000 BTU/Gal
$S_{resid.}$ 1.6%, 152,000 BTU/Gal

d. S = 2.5%, 8% Ash, 13,000 BTU/#

TABLE 2-3

EMISSIONS OF OXIDES OF NITROGEN FROM INDUSTRIAL BOILERS AND HEATERS

Source	Heat Input Range millions of Btu/hr	Range of NO_x Conc. in Flue Gases ppm by vol.	Av. NO_x Conc. ppm by vol.	NO_x Emission Factors av. lb per million Btu
Small oil heaters	Less than 60	20 to 100	47	
Natural gas				0.06
Fuel oil				0.33
Large refinery heaters	90 to 200	25 to 137	59	
Natural gas				0.25
Fuel oil				0.52
Small boilers (less than 500 hp)	Less than 20			
Natural gas		5 to 92	33	0.14
Fuel oil		15 to 387	122	0.49
Large boilers (500 hp and larger)	20 to 90			
Natural gas		45 to 149	91	0.28
Fuel oil		214 to 282	258	0.62
Power plant steam generators	200 to 2000			
Natural gas		75 to 320	205	0.36
Fuel oil		275 to 600	420	0.78

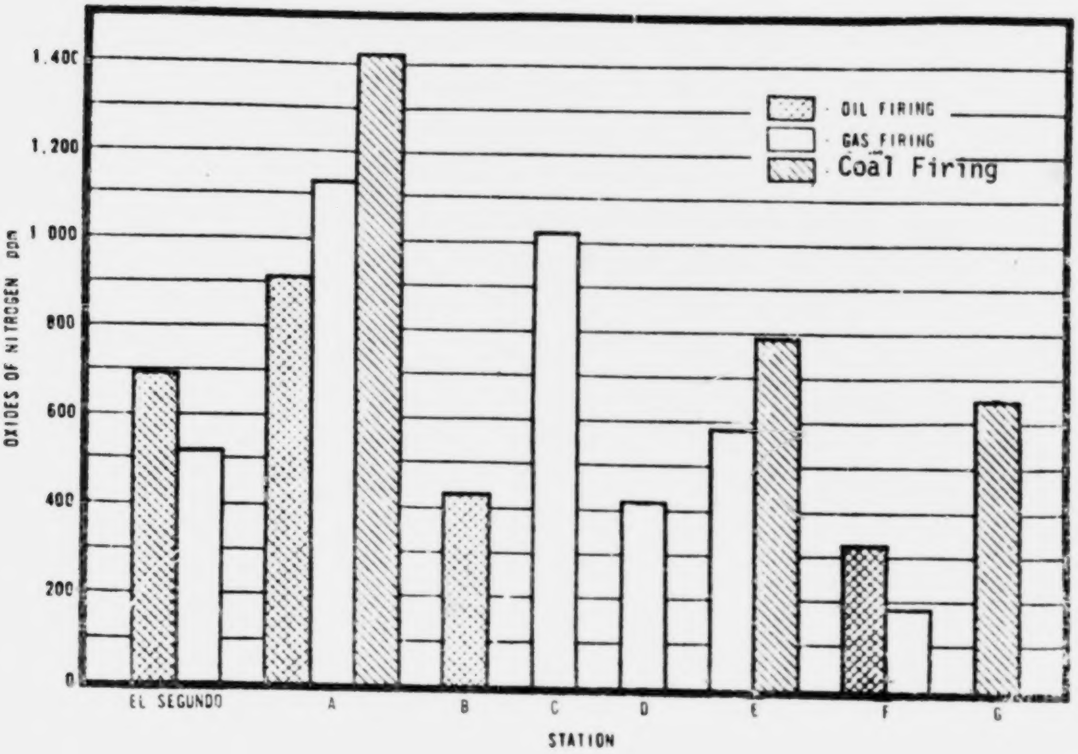

Figure 2-1. Oxides of nitrogen concentrations in gases from various gas-fired, oil-fired, and coal-fired steam generators.

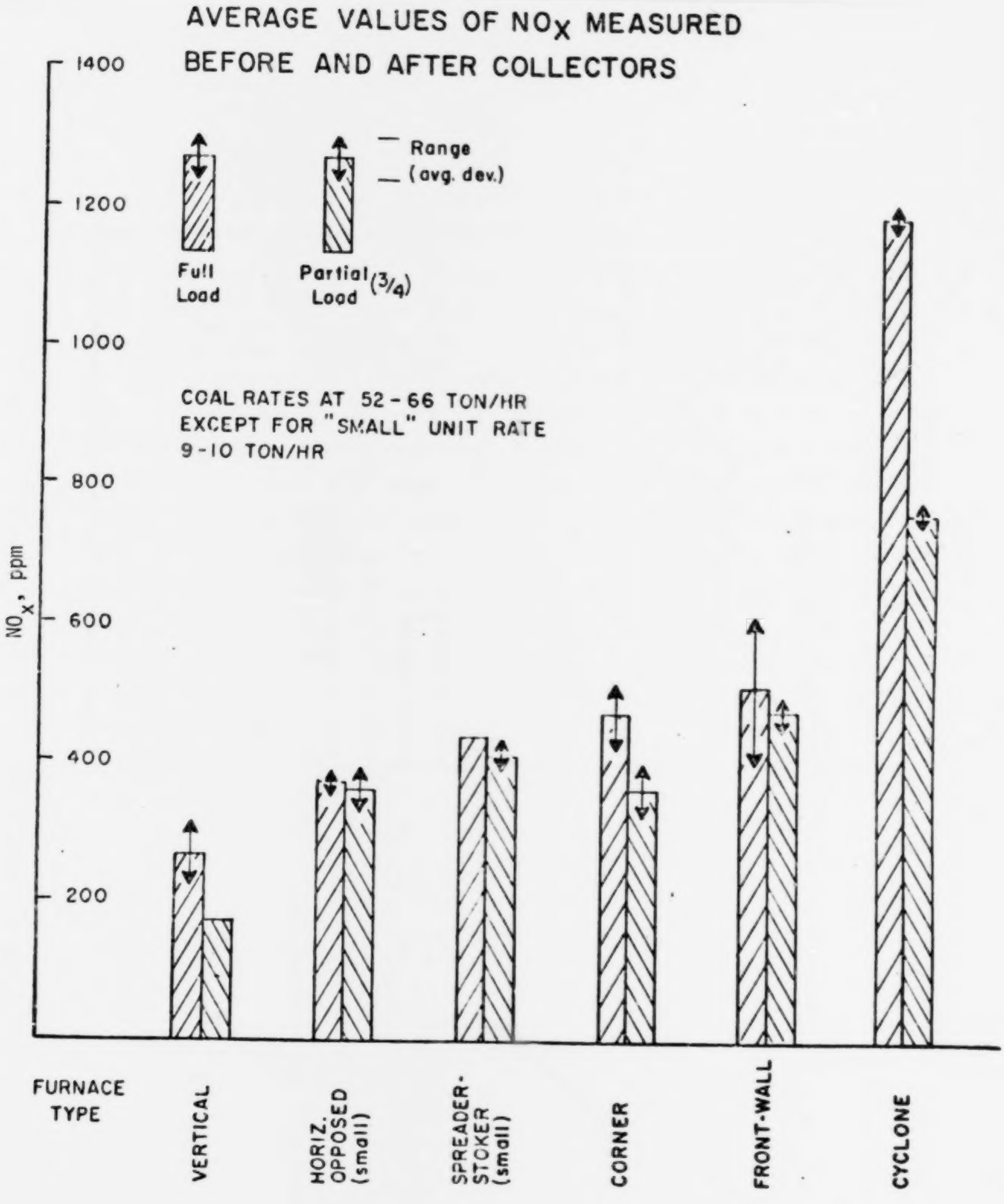

Figure 2-2. NO$_X$ Emission Concentration as a Function of Furnace Type (Coal). (Data from Cuffe and Gerstle)

technique of Barnhart and Diehl (464) has been utilized to achieve marked reduction in NO_x concentration (Table 2-4).

TABLE 2-4

EFFECT OF TWO-STAGE COMBUSTION ON NO_x CONCENTRATIONS
FROM A LARGE STEAM GENERATOR AT NORMAL FULL LOAD
(Barnhart and Diehl)

Fuel	NO_x Concentration All Air Through Burners ppm by vol.	Two-Stage Combustion Air Through Burners % of Theoretical*	NO_x ppm by vol.	Reduction %
Oil and gas combined	525	95	385	27
Oil	580	90	305	47

Other techniques for reduction of NO_x concentrations, by modification of combustion conditions, such as flue gas recirculation (518), are under investigation. In general, these techniques do not affect NO_x concentrations or potential interferences very radically from the point of view of analytical determinations.

SO_x control processes summarized in Volume I of this report are not very efficient for NO_x control (see Section 3, following) but do affect the flue gas environment, notably in reduction of particulate and SO_2 content of the effluent. NO_2/NO_x ratios may be significantly altered by scrubbing or catalytic oxidation (Monsanto Catox) processes designed for SO_x control. As detailed in Section 3, N_2O and HNO_3 (g) species may appear where residence times are increased.

2.4 Interferences

Particulate matter, as discussed in Volume I, is an impediment to analysis and must be removed by filtration during sampling. Since both NO and NO_2 are relatively low boiling materials, adsorption should not be an important factor, particularly for the principal component, NO.

Catalytic (heterogeneous) oxidation is of possible importance only where the individual oxides are sought, and is probably not significant given the short residence times in both the duct and sampling probe.

The substance of greatest significance for potential interference in NO_x determination is sulfur dioxide. SO_2, as is shown subsequently, is a direct interference for some analytical methods and a complication in others. Thus, gas-fired equipment, and high efficiency SO_x control equipment present interesting possibilities for application of simplified methods. It should be noted that the PDS* method for NO_x is not affected by SO_2 at levels ordinarily encountered.

Other gaseous species (CO_2, O_2, CO, HCl, hydrocarbons, organic acids, etc.) may produce interferences in the analytical determination of NO_x. Since these effects are specific, they are discussed individually for each method considered.

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*Phenol disulfonic acid

3. CHEMISTRY OF NITROGEN OXIDES IN FLUE GASES

3.1 Gas Phase Equilibria and Kinetics

3.1.1 General

There are seven oxides of nitrogen reported in the literature, namely:

N_2O	nitrous oxide
NO	nitric oxide
N_2O_3	dinitrogen trioxide
NO_2	nitrogen dioxide
N_2O_4	dinitrogen tetroxide
N_2O_5	dinitrogen pentoxide
NO_3	nitrogen trioxide

With the exception of NO_2, which is red-brown, the oxides are colorless in the gas phase. The existence of the oxides NO_3 and N_2O_3 has been questioned but there is now sufficient evidence that they do exist in the gas phase. The chemistry and equilibrium of the oxides of nitrogen are reviewed here to establish ranges and limitations of chemical methods of sampling and analysis of gaseous pollutants from combustion sources. The temperature and concentration ranges are far different from those of nitric acid manufacturing (602) so that the oxides of importance may be different in a flue gas environment.

The values of the equilibrium constants for the formation of the nitrogen oxides from the elements over the temperature range 400-2000°K are presented in Figure 3-1 (488). The three most stable oxides are NO, NO_2, and N_2O but all are in low concentrations ($< 10^{-2}$ atm) at equilibrium in flue gases. For a flue gas containing 0.8 atmosphere N_2 and 0.03 atmosphere O_2, the concentrations (in atmospheres) of these three nitrogen oxides are shown in Figure 3-2. Since the total concentration of nitrogen oxides is very small, the N_2 and O_2 levels are essentially unchanged by reaction and each oxide species concentration was

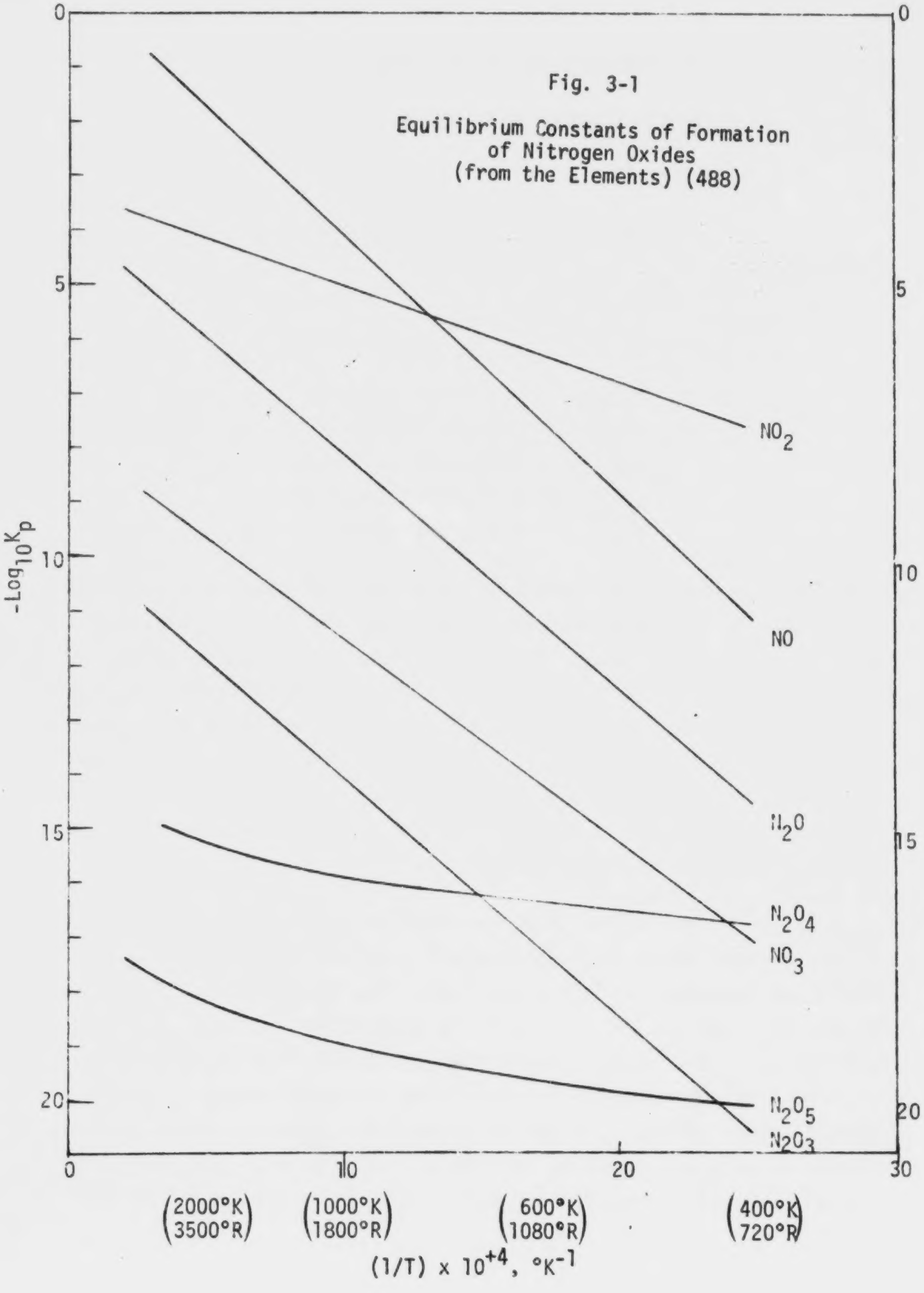
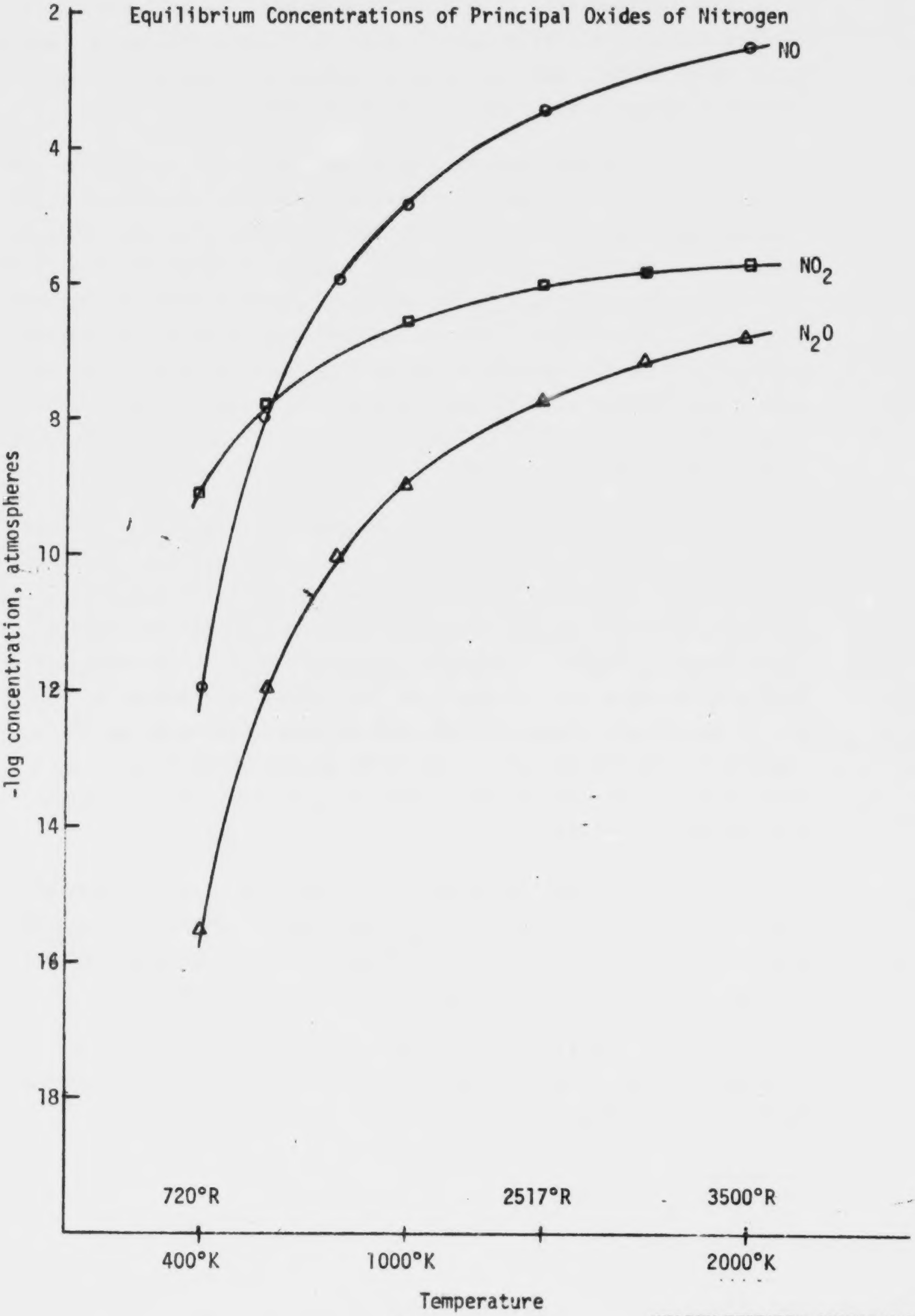


Fig. 3-1

Equilibrium Constants of Formation of Nitrogen Oxides (from the Elements) (488)

Figure 3-2

Equilibrium Concentrations of Principal Oxides of Nitrogen



calculated independently.[*] At high temperatures, the only oxide of significance is NO which is present in concentrations > 1000 ppm at temperatures above 1600°K. Over the range of combustion temperatures, NO_2 reaches a few parts per million ($\sim$ 5 ppm at 2000°K).

As the combustion gases are cooled the equilibrium concentrations of the nitrogen oxides are decreased but the actual concentrations may remain high because of kinetic limitations. For instance, the rates of decomposition of NO and NO_2 to the elements are slow so that concentrations of nitrogen oxides in excess of equilibrium at sampling temperature are expected. The rate of formation of NO may be significantly increased by reaction of oxygen with bound nitrogen in the fuel. Little quantitative work has been done (567,568) but nitrogen in fuel (e.g., coal) is apparently of major importance in the rate of NO production at lower temperatures (569).

The nitric oxide in the combustion products can react with excess oxygen to form NO_2 as the gases are cooled and the NO_2 may then dimerize to N_2O_4 at low temperatures (25-300°C) (Figure 3-3). However, in combustion gases the concentration of N_2O_4 is very small at all temperatures. Further, N_2O may be present since it is the next most stable oxide other than NO and NO_2. The dinitrogen trioxide is not present at appreciable concentrations even at room temperature but forms rapidly from NO and NO_2 and is the oxide species which is absorbed to form nitrous acid. The higher oxides, N_2O_5 and NO_3, are not present in significant concentrations.

Besides the oxides of nitrogen, reaction products of nitrogen oxides and water vapor (HNO_3, HNO_2) may be present. If liquid water is present, these exist in both the liquid and gaseous phase. Nitrous acid vapor is present at very low concentrations.

The oxides are discussed in the following sections in more detail, including significant kinetic and equilibria calculations. Equilibria including water are discussed in Section 3.1.3.

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[*] See Section 3.1.3 for equilibria including H_2O.

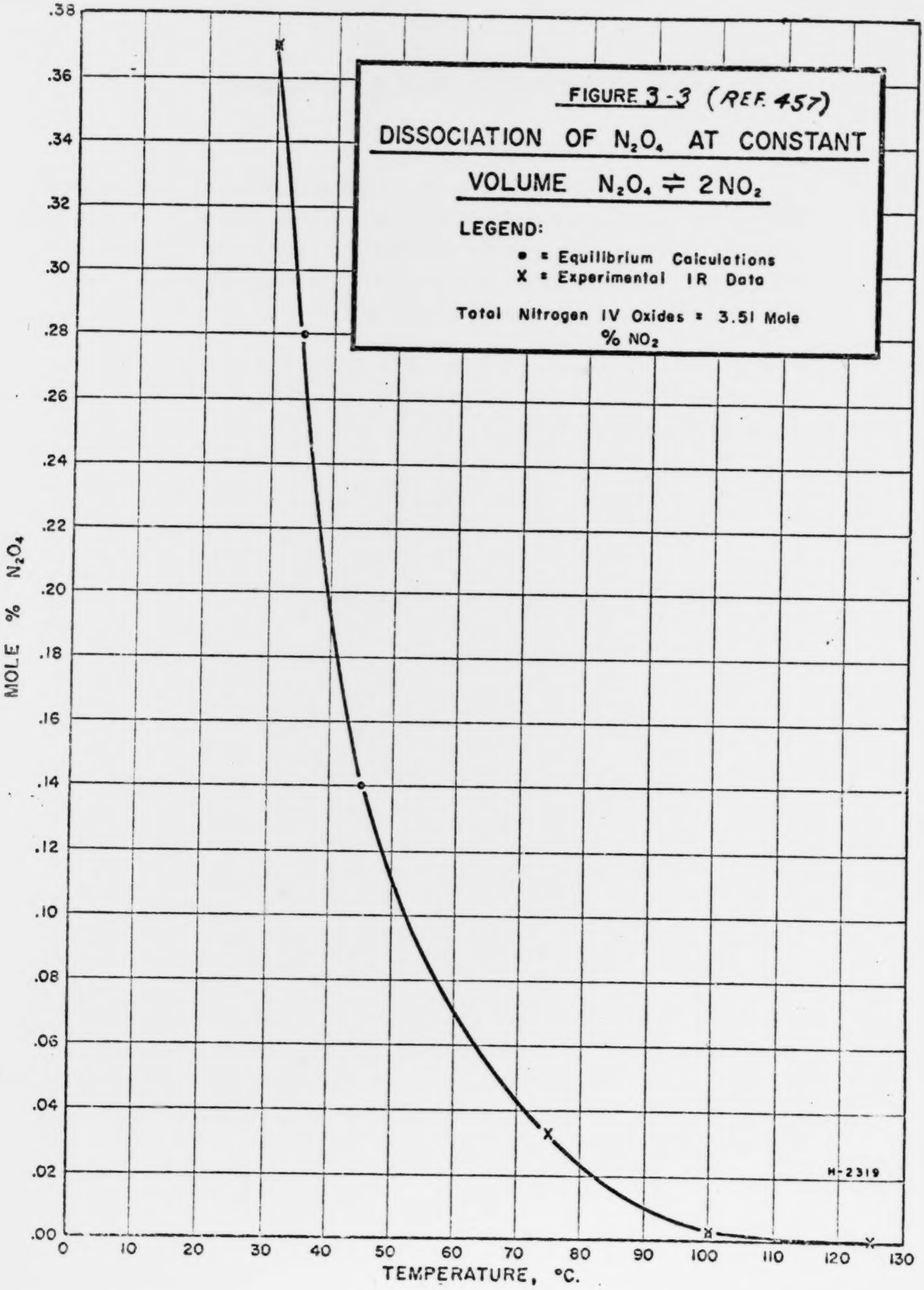

FIGURE 3-3 (REF. 457)

DISSOCIATION OF N_2O_4 AT CONSTANT VOLUME $N_2O_4 \rightleftharpoons 2NO_2$

3.1.2 Equilibria and Kinetics Among the Oxides

3.1.2.1 Nitric Oxide, NO

Nitric oxide is the only oxide of nitrogen present in significant concentrations at flue gas temperatures. Thermodynamically, the oxide is very unstable and should dissociate to the elements at all temperatures encountered in a collection or sampling system. The equilibrium for the formation of nitric oxide:

$$1/2\ N_2 + 1/2\ O_2 = NO$$

has an equilibrium constant

$$Kp = \frac{p_{NO}}{\left(p_{N_2}\right)^{1/2}\left(p_{O_2}\right)^{1/2}}$$

which varies with temperature as follows (488):

Temperature °K	$\log_{10} K_p$
298	-15.171
500	- 8.783
1000	- 4.062
1500	- 2.487
2000	- 1.699
2500	- 1.227
3000	- 0.913

However, the rate of dissociation is extremely slow:

$$-\frac{d(NO)}{dt} = 4.1 \times 10^{13}\ e^{-\frac{91,600}{RT}}\ (NO)$$

where T is in °K and the rate is expressed as g moles/cc-sec (444). At temperatures below 1500°K this rate is negligible at the low concentrations of nitric oxide normally present in stack gases. A more detailed discussion of NO formation and decomposition is given in Section 3.1.4, Kinetics of Formation of NO.

Further, the reaction of NO with other gases (444) such as H_2 and hydrocarbons is quite slow. However, NO can react with O_2 to form NO_2 at slow but significant rates.

3.1.2.2 Nitrogen Dioxide, NO_2

Nitrogen dioxide, like NO, is an unstable oxide and thermodynamically should decompose to the elements. However, the rate is negligibly slow. At low temperatures, the nitric oxide present in stack gases can react with oxygen to form NO_2 by the reaction:

$$NO + 1/2\ O_2 = NO_2$$

The equilibrium constant for this reaction

$$K_p = \frac{P_{NO_2}}{P_{NO}\left(P_{O_2}\right)^{1/2}}$$

is given below (488):

Temperature °K	$\text{Log}_{10} K_p$
298	6.194
500	2.114
1000	-0.938
1500	-1.951
2000	-2.453

Thus, at temperatures below about 1000°K, NO_2 is more stable than NO and the nitric oxide present in stack gases samples will form NO_2 provided enough time is available. Near room temperature (up to 500°K) essentially all of the NO will form NO_2 (at equilibrium).

The kinetics of the reaction of NO with O_2 is unusual in several ways. The reaction proceeds homogeneously in the gas phase at a measurable but slow rate. It goes faster at lower temperatures and proceeds by termolecular kinetics, with a rate proportional to the square of the NO partial pressure times the partial pressure of O_2.

$$\frac{d(p_{NO_2})}{dt} = k\, p_{NO}^2\, p_{O_2}$$

Expressing the partial pressures in atmospheres and time in seconds, the value of k found by Bodenstein and reported by Chilton (602) is

$$\log_{10} k = \frac{641}{T} - 0.725$$

where T is in °K.

In order to gain some insight into the times required for oxidation, the above rate expression can be integrated. The time in seconds is (602):

$$t = \frac{2}{k\left[2(p_{O_2}) - p_{NO}\right]}\left[\frac{x}{p_{NO}(1-x)} - \frac{1}{2(p_{O_2}) - p_{NO}}\log_e\left(\frac{2p_{O_2} - p_{NO_x}}{2p_{O_2}(1-x)}\right)\right]$$

where p refers to the initial partial pressures of the species in atmospheres, x is the fraction of the initial NO converted to NO_2 and t is in seconds. For a stack gas containing 1000 ppm NO and 3% O_2, at 300°K, 10% of the NO is converted to NO_2 in 144 seconds and 50% is converted in 1283 seconds, or about 21 minutes. Alternatively, one may say that only a small amount (about 1-2 ppm) of the NO is converted to NO_2 in 10 seconds.

At 450°K, the rate constant, k, is 5, so that the times involved would be four times longer than at 300°K.

Thus, the NO in a stack gas sample maintained at or slightly above room temperature will be slowly converted to NO_2; if several hours are allowed most of the NO is converted, but in seconds, essentially none is converted.

3.1.2.3 Dinitrogen Tetroxide, N_2O_4

The nitrogen dioxide present in a gaseous mixture may dimerize to the dinitrogen tetroxide, N_2O_4. The rate of the reaction

$$NO_2 = 1/2\ N_2O_4$$

is very rapid in both directions so that NO_2 is in equilibrium with the dimer. For the above reaction, the equilibrium constant is:

$$K_p = \frac{\left(p_{N_2O_4}\right)^{1/2}}{p_{NO_2}}$$

and has the following values as a function of temperature (488):

Temperature °K	$Log_{10}\ K_p$
298	0.417
400	-0.851
500	-1.584

For a gas which contained initially 1000 ppm NO all of which was oxidized to NO_2 only a small portion of the oxide would be in the dimer form. For example, at 298°, $K_p = 2.61$ and the N_2O_4 would be about 6.6 ppm and the NO_2, 987 ppm. The fraction as N_2O_4 is small but may be significant in collection since it is the dimer which is rapidly absorbed in water to form nitric acid, releasing nitric oxide (see Section 3.3).

3.1.2.4 Dinitrogen Trioxide, N_2O_3

The dinitrogen trioxide, which is the anhydride of nitrous acid, is formed by the reaction of NO and NO_2 in the gas phase. The equilibrium constant for this reaction is:

$$K_p = \frac{p_{N_2O_3}}{p_{NO}\ p_{NO_2}}$$

and has the following dependence on temperature (488):

Temperature °K	$\mathrm{Log}_{10} K_p$
298	-0.278
400	-2.087
500	-3.139

where the oxides NO and NO_2 are at low concentration ($\leq$ 1000 ppm), the total amount of N_2O_3 is very small. For example, if NO_2 and NO are present in equimolar quantities of 500 ppm, then $p_{N_2O_3}$ = 0.132 ppm.

The dinitrogen trioxide is still of importance since it is the species which is absorbed in water to form nitrous acid (HNO_2) from an equimolar mixture of NO and NO_2. The nitrogen oxides, NO and NO_2, react rapidly to form N_2O_3 which is then absorbed in the water. Obviously, at low oxide concentrations, the rate of absorption will be low because of the extremely low equilibrium partial pressure of N_2O_3.

3.1.2.5 Nitrogen Trioxide and Dinitrogen Pentoxide, NO_3 and N_2O_5

The concentrations of NO_3 and N_2O_5 are extremely low under all conditions of interest and need not be considered further.

3.1.2.6 Nitrous Oxide, N_2O

Nitrous oxide, N_2O (laughing gas) is a non-toxic oxide of nitrogen which supports combustion almost as well as oxygen. The equilibrium constant for the reaction:

$$NO_2 = 1/2\ N_2O + 3/4\ O_2$$

is

$$K_p = \frac{\left(p_{N_2O}\right)^{1/2} \left(p_{O_2}\right)^{3/4}}{p_{NO_2}} .$$

This equilibrium constant varies with temperature as follows (488):

Temperature °K	$\log_{10} K_p$
298	-0.147
400	+0.215
500	+0.438

The equilibrium constant is approximately unity over the range of interest in sampling and analysis. For a gas which originally contained 1000 ppm NO and 3% O_2 at 298°K and was allowed to react to NO_2 and N_2O, the equilibrium concentration of NO_2, O_2 and N_2O would be:

Compound	Concentration (ppm)
NO	< 1
NO_2	854
N_2O	73
O_2	29,790

At 400°K (starting with the same initial mixture of gases), the gaseous species in equilibrium would be:

Compound	Concentration (ppm)
NO	< 1
NO_2	616
N_2O	192
O_2	29,790

Provided there is a kinetic route to N_2O there will be a significant fraction of the oxides in the form of N_2O. At these low temperatures it is unlikely that a homogeneous gas phase route is possible. However, some of the older preparations of N_2O suggest a possible route. Priestly (604) formed N_2O by passing NO over moist iron fillings. Also, nitrous oxide can be found in the presence of sulfur dioxide by the reaction (604):

$$2NO + SO_2 + H_2O = H_2SO_4 + N_2O$$

Each of these mechanisms is possible in a sampling unit or in the stack system of a combustion device. Recent work on either of these reactions appears to be lacking.

3.1.3 Equilibria and Kinetics Among the Oxides and Oxyacids

In addition to the oxides of nitrogen, there are two oxyacids, nitrous acid, HNO_2 and nitric acid, HNO_3. Both may be present in the gas phase or in aqueous solution.

3.1.3.1 Nitrous Acid, HNO_2

Nitrous acid is formed in aqueous solutions when N_2O_3 dissolves. Nitrous acid is unstable in solution and decomposes to nitric acid and nitric oxide unless the solution is cool and alkaline.

$$3HNO_2 \rightarrow HNO_3 + 2NO + H_2O$$

Nitrous acid can exist in the vapor state in equilibrium with the oxides of nitrogen and water vapor. The equilibrium constant for the reaction:

$$NO + NO_2 + H_2O = 2HNO_2$$

is

$$K_p = \frac{\left(p_{HNO_2}\right)^2}{\left(p_{NO}\right)\left(p_{NO_2}\right)\left(p_{H_2O}\right)}$$

and varies with temperature as follows (488):

Temperature °K	$Log_{10} K_p$	
	cis(HNO_2)	trans(HNO_2)
298	-1.212	-0.496
400	-2.789	-2.257
500	-3.718	-3.292

At higher temperatures, nitrous acid vapor decomposes to the oxides and water vapor. Near room temperature a calculation of the amount of HNO_2 vapor present at equilibrium requires that the oxides NO, NO_2, N_2O_4, as well as nitric acid vapor, HNO_3, be determined simultaneously.

3.1.3.2 Nitric Acid, HNO_3

Nitric acid exists in the vapor phase and dissolves in water up to 68 wt %. Decomposition of nitric acid is very slow and several days time is required to approach equilibrium at room temperature. The equilibrium composition of HNO_3 vapor can be calculated from the equation:

$$H_2O + 2NO_2 + 1/2\ O_2 = 2HNO_3$$

for which the equilibrium expression is:

$$K_p = \frac{\left(p_{HNO_3}\right)^2}{\left(p_{NO_2}\right)^2\left(p_{H_2O}\right)\left(p_{O_2}\right)^{1/2}}$$

Nitric acid vapor is stable at room temperature but decomposes at higher temperatures as the values in the following table show (488):

Temperature °K	$Log_{10}\ K_p$
298	+3.838
400	-0.334
500	-2.784

The presence of other gases (NO, NO_2, N_2O_4 and HNO_2) must be accounted for in doing the simultaneous equilibrium calculations.

Nitric acid is normally formed in aqueous solution by passing a gas containing NO_2 through water. Each three moles of nitrogen dioxide forms two moles of HNO_3 and a mole of NO, which must be reoxidized to NO_2 in the gas phase:

$$3NO_2 + H_2O = 2HNO_3 + NO$$

Determination of the equilibrium of the oxyacids in the vapor require the calculation of several simultaneous equilibria. Several specific examples will be considered.

For a flue gas mixture at one atmosphere and 298°K which originally contained NO, O_2, H_2O and N_2 at partial pressures 0.001, 0.03, 0.08 and 0.889 atmospheres, respectively, the amount of HNO_2 vapor can be estimated. Under these conditions most of the NO will be converted (at equilibrium) to NO_2 with a small amount as N_2O (see N_2O discussion). Consequently, the partial pressure of HNO_2 will be negligibly small because the partial pressures of the species on the left side of the equation:

$$NO + NO_2 + H_2O = 2HNO_2$$

are small (the amount of NO is extremely small). For example, using the concentrations developed in the discussion of N_2O and a value 0.1 for the (average between cis and trans) equilibrium constant of the above reaction forming HNO_2 and setting the partial pressure of NO at 10^{-6} (high estimate) the partial pressure of HNO_2 is less than 1 ppm. Further nitric acid vapor will consume some of the NO_2 so that this is a high estimate for HNO_2. Similarly, for other temperatures and similar concentration ranges the amount of HNO_2 in the vapor can be neglected in sampling.

However, the amount of HNO_3 will be far more important if equilibrium is assumed among the oxides and oxyacids since the equilibrium constant for its formation from NO_2, H_2O and O_2 is very favorable at low temperatures. For instance, at 298°K the equilibrium composition of the nitrogen oxides and oxyacids at one atmosphere pressure from a mixture originally containing 1000 ppm NO, 3% O_2 and 8% H_2O is approximately:

Compound	Concentration (ppm)
HNO_3	905
NO_2	94
N_2O	1

All other fixed nitrogen species are negligible. As in all of the previous calculations, decomposition of any of the species to the elements has been neglected.

A more interesting calculation is one in which the above initial mixture is allowed to reach equilibrium at 400°K and 1 atm. The HNO_3 is less stable so that all three species, NO_2, H_2O, and HNO_3 are present in significant concentrations.

The computer program DEQL (see Appendix 3) was utilized to conduct these equilibrium calculations. The results are shown in detail in the computer printout, Table 3-1; the last four (data) lines contain the species and concentrations. Major nitrogen-oxygen species concentrations are summarized below.

Compound	Concentration (ppm)
NO_2	589
HNO_3 (g)	47
N_2O	182
NO	0.8

Provided kinetic routes exist for convertine NO_2 to N_2O and HNO_3, a significant error could be introduced in stack analysis by the presence of these species. Deilin (449) has reported small amounts of N_2O in stack gases.

3.1.4 Kinetics of Formation of NO

3.1.4.1 NO Kinetics

The concentrations of nitrogen oxides in stack gases reported in the literature are below those calculated for equilibrium at flame temperature but above those in equilibrium at stack gas temperature indicating that kinetics are important. The kinetics and mechanism of NO formation are not simple but are well established and are in close agreement with the model and results originally published and discussed in detail by Zeldovish (448). The major results and conclusions of his work are discussed here.

(a) The rate of NO formation (except from nitrogen already fixed in the fuel) proceeds so much less rapidly than the

TABLE 3-1

Computer Printout of Equilibrium Concentrations of Nitrogen Compounds in a Flue Gas at 400°K

```
>fildef 2 dsk t400 data
R; T=0.26 17.25.46
>$ deql
EXECUTION BEGINS...
 GAS COMPOSITION FOR NO,H2O,O2,N2 FEED
 T=400. KELVIN          TOTP= 1.000
 FEED NO=  0.0010        O2=  0.0300       H2O=  0.0800       N2=  0.8890


 REACTION   LOG OF K EQUILIBRIUM CONSTANT
      1       3.6290          0.426E 04
      2      -0.1660          0.682E 00
      3       0.4300          0.269E 01
      4      -0.8510          0.141E 00
      5      -3.0760          0.838E-03
      6      -5.1330          0.735E-05
      7      -5.7160          0.192E-05
      8      -9.6690          0.213E-09
 GAS COMPOSITION WITH ERROR IN K NOT MORE THAN, 0.001       ITERATIONS ^
   81        CYCLES      4 TEMPERATURE 400. KELVIN


  I          ABS VALUE (KCALC/K -1.0)
  1                  0.954E-06
  2                  0.989E-03
  3                  0.858E-05
  4                  0.987E-03
  5                  0.793E-03
  6                  0.666E-05
  7                  0.519E-05
  8                  0.808E-03
 SUM PARTIAL PRESSURES=    1.00        SUM N=  0.001        SUM H=  0.160 ^
    ' SUM O=  0.141
      PNO       PNO2        PO2        PH2O       PHNO3       PN2O

    0.301E-06 0.589E-03 0.293E-01 0.800E-01 0.472E-04 0.182E-03


     PN2O4     PHNO2      PN2O5      PN2O3       PNO3       PN2

    0.687E-08 0.336E-06 0.439E-12 0.335E-11 0.217E-13 0.889E 00
IHC002I STOP      0
R; T=3.12 17.27.00
>
```

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combustion reactions that it takes place after the combustion process is complete and is purely thermal in nature. Several corollaries follow: the rate of NO formation does not depend on the chemical nature of the fuel but on its heat of combustion; the rate depends on the concentration of N_2 and O_2 remaining after combustion (excess O_2); preheating the fuel or air is equivalent to increasing the heat of combustion.

(b) The amount of NO formed is always less than the equilibrium amount at peak flame temperature due to the finite rate of the forward reaction and to the reverse reaction $NO \rightarrow 1/2\ N_2 + 1/2\ O_2$ as the combustion products cool.

(c) The activation energies of NO formation and dissociation are very large, 129 and 86 kcal, respectively.

(d) The forward reaction proceeds via a chain mechanism. Oxygen is in equilibrium with oxygen atoms by the reaction:

$$O_2 + M \underset{k_2}{\overset{k_1}{\rightleftarrows}} O_2 + M$$

where M is any "third body." The oxygen atom then participates in the exchange reactions.

$$O + N_2 \underset{k_4}{\overset{k_3}{\rightleftarrows}} NO + N$$

$$N + O_2 \underset{k_6}{\overset{k_5}{\rightleftarrows}} NO + O$$

The reaction between oxygen atom and nitrogen molecule is rate limiting and has an activation energy of 68 kcal. By assuming that O and N concentrations reach steady state, Zeldovich predicted a rate expression:

$$\frac{d(NO)}{dt} = \frac{2\sqrt{K_1(O_2)}}{k_5(O_2) + k_4(NO)} \left\{ k_3k_5(N_2)(O_2) - k_4k_6(NO)^2 \right\}$$

where K_1 is k_1/k_2, the equilibrium constant for oxygen dissociation. Further, k_4 and k_5 are of the same magnitude so that if $(O_2) >> (NO)$, the rate expression becomes:

$$\frac{d(NO)}{dt} = \frac{2\sqrt{K_1}\ k_3}{K_2\sqrt{O_2}} \left\{ K_2(O_2)(N_2) - (NO)^2 \right\}$$

where K_2 is the equilibrium constant for the overall reaction

$$N_2 + O_2 \rightleftarrows 2NO$$

(e) The rate expression then becomes, numerically

$$\frac{d(NO)}{dt} = \frac{5 \times 10^{11}\ e^{-\frac{86,000}{RT}}}{\sqrt{O_2}} \left\{ 21\ e^{-\frac{43,000}{RT}} (N_2)(O_2) - (NO)^2 \right\}$$

where t is in seconds, and concentration in gram moles per liter. This expression was tested over a wide range of concentrations including very low oxygen levels where the proposed chain mechanism might be questionable and over the temperature range 2000-3000°K.

3.1.4.2 Discussion of Zeldovich Kinetics

Both the forward and reverse reactions have very large activation energies, 129 and 86 kcal, respectively. Consequently, the rates of both reactions become appreciable only at high temperatures, i.e., at 2000°K

$$e^{-\frac{129,000}{RT}} = e^{-32.6}$$

For comparison, the same value of the exponential term would be obtained for a reaction with an activation energy of 20 kcal at 323°K (50°C). At about 1300°K the reverse reaction "freezes," i.e., the reaction is so slow that for residence times of a few seconds, no appreciable change in NO concentration occurs. Since the reactions proceed rapidly only at high temperatures, the temperature sensitivity of both reactions is relatively small despite the large activation energies. The ratio of the reaction rates at two temperatures, T_1 and T_2, is approximately

$$e^{-\frac{E\Delta T}{RT^2}}$$

where ΔT is T_2-T_1 and T is the average of T_1 and T_2. Thus, at 2000°K for an activation energy of 129 kcal, the reaction rate doubles with an increase in temperature of 425°C. (Equivalently, the rate changes 17.7% for a 10°C change in temperature.) The reverse reaction is less temperature sensitive and an increase of 64°C will double the rate at 2000°K.

The rate of formation of NO depends on the square root of the oxygen concentration remaining after combustion (excess oxygen) so that a doubling of the oxygen concentration changes the forward rate by 1.414. At peak flame temperatures (∿ 2200°K), an increase in temperature of about 26°C would be required to increase the rate an equivalent amount (41.4%). At lower temperatures a smaller change in temperature is needed for the same percentage change in rate.

Additional factors to be considered in NO kinetics are the rate of cooling of the combustion gases and the maximum flame temperature. At low flame temperatures (low heat of combustion, no preheat, diluent added, etc.) and with rapid cooling, the amount of NO formed will be low and far less than the equilibrium yield at flame temperature. The reverse reaction can be neglected and rapid cooling of the combustion gases will "freeze" the forward reaction. At high flame temperatures and with slow cooling, the NO yield is again low. Large amounts of NO are produced initially but the reverse reaction occurs as the gases cool and the final yield of NO, determined by the temperature at which the reverse reaction freezes, is very low. Obviously, in this case the NO level is independent of maximum flame temperature. Between these two limits the nitrogen oxide yield goes through a maximum. Zeldovich showed this maximum to be 60-70% of the equilibrium yield at peak flame temperature in his system.

An accurate calculation of NO produced in a particular combustion device depends on a knowledge of the temperature-time and concentration-time (N_2, excess O_2) history of each parcel of the post-combustion gases. With this information, the nitric oxide rate expression can be integrated to find the yield of nitric oxide. Generally, one does not have the desired spatial and temporal distribution of temperature and concentration and approximate (e.g., time average, plug flow) profiles are assumed.

The activation energies recommended by Zeldovich were 129 ± 10 and 86 ± 10 kcal for formation and dissociation of NO, respectively. His data showed values of 125 ± 10 and 82 ± 10 but he raised the average values to account for non-uniform temperature distributions and to simplify his later calculations. The difference between the activation energy for the forward and reverse reaction is ∿ 43 kcal since the equilibrium constant for the reaction

$$N_2 + O_2 \rightleftarrows 2NO$$

is

$$K_1 = \frac{(p_{NO})^2}{p_{N_2}\, p_{O_2}} = 21.12\, e^{-\frac{43,260}{RT}}$$

More recent data (591-598) generally confirm the mechanism and kinetics of Zeldovich. However, the activation energies reported are higher than those of Zeldovich at high temperature (2000-3000°K) but less than those of Zeldovich at low temperature (1300-1600°K). For example, Glick, et al. (593) and Camac and Feinberg (591) report the activation energy of NO decomposition to be ∿ 92 kcal between 2300 and 3000°K whereas Kaufman and Kelso (594) and Wise and Frech (596,597) report values of 63.8 and 82 kcal, respectively, at temperatures around 1500°K. Most of these investigators report a ±5 kcal uncertainty associated with the activation energies. However, many stationary combustion devices operate between 1600 and 2000°K necessitating an extrapolation of the kinetic data with temperature. Although the data of the several investigators are quite close (about a two-fold variation) within the low (< 1600°K) and high (> 2300°K) temperature ranges, the activation energies reported will greatly affect the extrapolation into the intermediate temperature range of interest. Bortner and Golden (599) reviewed and correlated much of the data available through 1960 on reaction rate constants for species in high temperature air. They fitted curves through the data of several investigators between room temperature and 7000°K for the individual reactions involved in nitric oxide formation and decomposition. Their curves yield a forward rate expression for nitric oxide formation:

$$\frac{d(NO)}{dt} = 7 \times 10^{12}\, T^{1/2}\, e^{-\frac{135{,}700}{RT}}\, (N_2)(O_2)^{1/2}$$

where t is in seconds and concentrations in gram moles per liter.

Several of the reported rate expressions for nitric oxide formation are given in Table 3-2 with the temperature range over which the data were collected. In each case the rate expression is evaluated numerically at 2200°K to show the magnitude of variations that are to be expected upon extrapolation of these kinetic expressions.

The expressions of Bartok, et al. (444) and Bortner and Golden (599) (see Table 3-2) agree closely at 2200°K. These rate expressions are based on recent data of several investigators on the individual steps in the chain mechanism.* It is unlikely that data for combustion equipment could be used to select one of these two expressions

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*For a recent summary of the rate constants of the elementary steps in nitric oxide formation as well as those involving CO, CO_2, O_2 and H_2O, see reference (600) and for a very complete list and discussion, reference (601).

TABLE 3-2

COMPARISON OF NITRIC FORMATION RATE EXPRESSIONS

Investigator	Temperature Range °K	Forward Rate Constant*	Forward Rate Constant* at 2200°K
Camac & Feinberg (591)	2300-3000	$7 \times 10^{14} \exp\left(-\frac{134,300}{RT}\right)$	29.4
Glick, et al. (593) Bartok, et al. (603)	2000-3000	$9 \times 10^{14} \exp\left(-\frac{135,000}{RT}\right)$	31.05
Zeldovich (448)	2000-3000	$3.32 \times 10^{14} \exp\left(-\frac{129,000}{RT}\right)$	46.1
Bartok, et al. (444)	Recommended for stationary combustion	$3 \times 10^{14} \exp\left(-\frac{135,000}{RT}\right)$	10.35
Bortner & Golden (599)	Best fit 300-7000°K	$7 \times 10^{12}\, T^{1/2} \exp\left(-\frac{135,700}{RT}\right)$	10.80
Freedman & Daiber (592)	3000-4300	$1.01 \times 10^{25}\, T^{-3/2} \exp\left(-\frac{128,000}{RT}\right)$	8140
Kaufman & Kelso (594)	1300-1600	$5.49 \times 10^{13} \exp\left(-\frac{107,100}{RT}\right)$	1193

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*The rate constant is that value of k in the expression $+\frac{d(NO)}{dt} = k(N_2)(O_2)^{1/2}$ gr moles/cc-sec for the first five investigators (591,593,448,444,599), but is k in the expression $\frac{d\ NO}{dt} = k(N_2)(O_2)$ gr moles/cc-sec for the last two citations (592,594).

over the other. The two expressions are compared numerically at three temperatures (1000, 2200, and 3000°K) in Table 3-3. The expressions are close except at temperatures where the rate is insignificantly small.

TABLE 3-3

COMPARISON OF CALCULATED VALUES OF THE NITRIC OXIDE FORMATION RATE EXPRESSION OF BARTOK, ET AL. (444) AND BORTNER AND GOLDEN (599)

Investigator	1500°K	2200°K	3000°K
Bartok, *et al*. (444)	6.32×10^{-6}	10.35	5.88×10^{3}
Bortner and Daiber (599)	2×10^{-6}	10.80	6.85×10^{3}

Values reported are for k in the rate expression:

$$\frac{d(NO)}{dt} = k(N_2)(O_2)^{1/2} \text{ gr moles/cc-sec}$$

The values reported by Freedman and Daiber (592) and Kaufman and Kelso (594) are expressed for a bimolecular forward reaction. Obviously their values cannot be compared exactly to the other experiments since oxygen concentration affects the comparison. For a bimolecular rate constant of 5000 (about midway between those in Table 3-2) and for a chain mechanism rate constant of 10 [close to Bortner and Golden (599)], the oxygen partial pressure would have to be 0.1385 atm at 2200°K for the two rates to match exactly.

The rate of decomposition of NO to O_2 and N_2 is (444):

$$-\frac{d(NO)}{dt} = 4.1 \times 10^{13} e^{-\frac{91,600}{RT}} (NO)^2$$

3.1.5 Reaction with SO_2

A further complication in the kinetics and equilibrium of stack gases arises when SO_2 is present from the combustion of sulfur bearing fuels. The SO_2 will react with NO_2 to form SO_3 and NO

$$NO_2 + SO_2 = SO_3 + NO$$

The kinetics of this reaction are rapid (452,605), but reduction of NO_2 in flue gas samples by this reaction is slow since the concentrations of NO_2 and SO_2 are small. However, the rate of formation of NO by this reaction may well be faster than its rate of reoxidation by O_2.

3.1.6 Summary

Of the seven oxides and two oxyacids, only three of the oxides (N_2O, NO, NO_2) and one of the oxyacids (HNO_3) need be considered in flue gas analysis. At high temperatures (> 1000°K), only NO exists in significant concentrations; at lower temperatures (25-400°K), all four species may be important. Kinetic limitations prevent the dissociation of these species to the elements. However, the three oxides and HNO_3 may react slowly with each other and with O_2 and H_2O. Generally, only NO is expected to be present in significant amounts in stack samples at low temperatures since reaction rates are slow, but if long times (minutes to hours) are allowed, significant concentrations of all of the above species may be generated.

3.2 Reactions of NO_3^- and NO_2^- in Solution

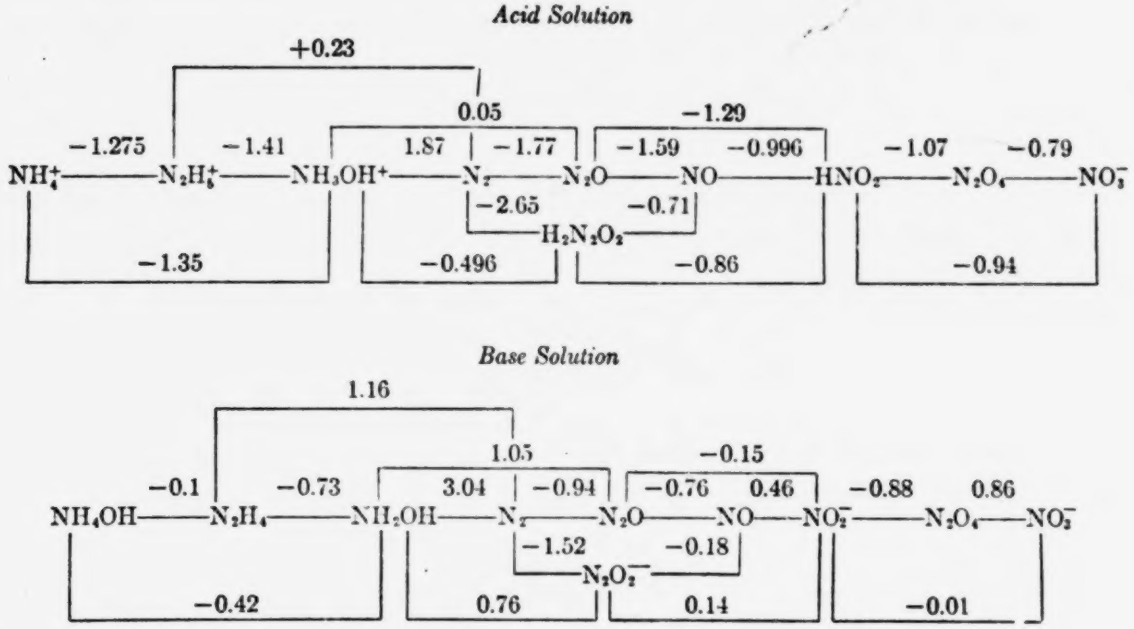
The redox potentials for various nitrogen couples in acid and basic solutions are given in Figure 3-4. Hydrolysis of the nitrogen oxides NO, NO_2, and N_2O_3 in aqueous solutions leads to the production of nitrite and nitrate ions.

The small positive standard free energy (ΔF°) for the reaction:

$$2HNO_2 \rightarrow NO + NO_2 + H_2O, \Delta F^\circ = 2.06 \text{ kcal}$$

Figure 3-4

Summary of Redox Potentials For Nitrogen Compounds (479)


Acid Solution
+0.23
0.05
−1.29
−1.275
−1.41
1.87
−1.77
−1.59
−0.996
−1.07
−0.79
NH₄⁺
N₂H₅⁺
NH₃OH⁺
N₂
N₂O
NO
HNO₂
N₂O₄
NO₃⁻
−2.65
−0.71
H₂N₂O₂
−1.35
−0.496
−0.86
−0.94
Base Solution
1.16
1.05
−0.15
−0.1
−0.73
3.04
−0.94
−0.76
0.46
−0.88
0.86
NH₄OH
N₂H₄
NH₂OH
N₂
N₂O
NO
NO₂⁻
N₂O₄
NO₃⁻
−1.52
−0.18
N₂O₂⁻⁻
−0.42
0.76
0.14
−0.01

reveals that there is an appreciable concentration of NO and NO_2 in equilibrium with the condensed phase (aqueous nitrous acid). A more important reaction is the disproportionation of nitrous acid:

$$3HNO_2 \rightarrow H^+ + NO_3^- + 2NO + H_2O,\ \Delta F° = -3.22 \text{ kcal}$$

The rate of the above reaction is slow in cold dilute HNO_2 solutions but becomes rapid if the solution is warmed.

The oxidation of nitrous acid to nitric acid (Figure 3-4) in acid solution requires a powerful oxidizing agent such as hydrogen peroxide or permanganate, since the oxidation potential is very high.

$$H_2O + HNO_2 \rightarrow NO_3^- + 3H^+ + 2e^-,\ E° = -0.94$$

Thermodynamically, nitrite may be oxidized in alkaline solution by comparatively weak oxidizing agents. The half reaction for the oxidation of nitrite is:

$$NO_2^- + 2OH^- \rightarrow NO_3^- + H_2O + 2e^-,\ E_B^\circ = -.01^*$$

The potential for oxidation by, for example, oxygen is, therefore, favorable (in alkaline solution).

$$NO_2^- + 1/2\ O_2 \rightarrow NO_3^-,\ E° = 0.39$$

Although there are contradictory statements in the literature on the ease of this reaction, slow kinetics prevent appreciable reaction (see 5.3.2 for discussion). The oxidation rate of nitrite by hydrogen peroxide has been reported to be directly proportional to the hydrogen ion concentration, and thus decreases rapidly as solution pH is increased (613,614).

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[*] Potential with respect to the hydrogen reference electrode in 1M OH^-, $E_B^\circ = 0.828$.

The reduction of nitrous acid by sulfur dioxide appears to be another example of slow kinetics. This reaction goes in acidic but not in basic media (479,613) although the thermodynamics of the reduction (to, say, hyponitrous acid) are favorable in both media.

In summary, collection of oxides of nitrogen in basic media appears to be effective kinetically in inhibiting many common oxidation and reduction reactions and thus preventing interferences. It is, however, not clear that inhibition will necessarily occur in all cases, since thermodynamically favored slow reactions are subject to both homogeneous and heterogeneous catalytic acceleration.

3.3 Chemistry of Absorption of Nitrogen Oxides in Aqueous Solutions

Sampling procedures presently utilized in the determination of NO_x may involve the following several major processes:

(1) oxidation of NO in the gas phase
(2) oxidation of NO in the liquid phase
(3) absorption of NO_2 and NO by aqueous solutions

In this section, we analyze the above reactions, insofar as possible, to permit a logical approach to the improvement of sampling procedures.

3.3.1 Gas and Liquid Phase Oxidation Rates of Nitric Oxide

NO_2 (or N_2O_4) has a far greater solubility in aqueous solution than NO (571,572). Upon absorption, NO_2 reacts with water to produce nitric and nitrous acids. The latter species decomposes readily in acidic solutions unless it is oxidized to nitric acid. On the other hand, little has been reported about possible reactions following absorption of pure NO in aqueous solution. There is evidence, however, (571, 573) that NO is absorbed rapidly in the presence of NO_2, in effect as N_2O_3, yielding nitrous acid. The data of Eagleton, Langer and Pigford (574) suggest that the rate of absorption of N_2O_3 is as much as ten times faster than that of NO_2 in 46% NaOH solution. This may be due to greater solubility of N_2O_3, faster liquid phase reaction rates, or, possibly both.

On the basis of the above brief description, it is concluded that even where liquid phase oxidation is employed, gas phase oxidation of NO must play a major role in the rate of overall absorption since the most likely absorbing species is either NO_2 and/or N_2O_3.

If the rates of absorption are rapid compared to the oxidation reaction rates, it is possible to estimate the minimum times necessary for the overall process of oxidation and absorption. This assumption is a fairly good one (see Section 3.3.2) since commercial absorption units used in the production of HNO_3 are designed (575) on this basis.

The gas phase oxidation of NO is a third order reaction that has been widely discussed in the literature (see, e.g., 576). The consumption rate of NO is given by:

$$-\frac{dP_{NO}}{dt} = k(P_{NO})^2 (P_{O_2}) \qquad (1)$$

where P_{NO} = partial pressure of NO, atm

P_{O_2} = partial pressure of O_2, atm

k = reaction rate constant = 23.2 atm^{-2} sec^{-1} at 86°F (571)

3.3.1.1 Oxidation Time for NO_2 Absorption

If we consider only NO_2 (or N_2O_4) as the absorbing species, the overall oxidation can be represented by:

$$2NO + O_2 \rightarrow 2NO_2 \qquad (2)$$

Provided that the total number of moles in the reaction system remains approximately constant (a good assumption for the low NO concentrations generally encountered in an effluent sample),

$$1/2\, dP_{NO} = dP_{O_2} \qquad (3)$$

Integrating Equation (3) gives:

$$1/2\,[(P_{NO})_{Initial} - P_{NO}] = [(P_{O_2})_{Initial} - P_{O_2}] \qquad (4)$$

so that,

$$P_{O_2} = 1/2\,[(2(P_{O_2})_{Initial} - (P_{NO})_{Initial}) + P_{NO}] \qquad (5)$$

Substitution of (5) into (1) therefore results in

$$-\frac{dP_{NO}}{(P_{NO})^2\,[P_{NO} + (2(P_{O_2})_{In} - (P_{NO})_{In})]} = \frac{k}{2}\,dt \qquad (6)$$

Equation (6) is readily integrated to give:

$$\frac{1}{P_{NO}} - \frac{1}{(P_{NO})_{In}} + \frac{1}{[2(P_{O_2})_{In} - (P_{NO})_{In}]} \ln \left[\frac{(2P_{O_2})_{In}\,(P_{NO})}{(P_{NO})_{In}\,(2P_{O_2})_{In} - (P_{NO})_{In} + P_{NO}} \right]$$

$$= \frac{k}{2}\,[(2P_{O_2})_{In} - (P_{NO})_{In}]\,t \qquad (7)$$

Considering a typical flue gas to contain 400 ppm NO and 5% O_2, Equation (7) may be directly applied to estimate oxidation times necessary for the production of different final NO compositions. The results of such computations are given in Table 3-4.

It is evident that if NO_2 (or N_2O_4) is the absorbing species, a minimum oxidation time of about 30 hours is required if the amount of NO_2 absorbed is to be within 2-1/2% of the amount of NO sampled.

TABLE 3-4

COMPUTED OXIDATION TIMES FOR TYPICAL FLUE GAS SAMPLES
Initial (NO) = 400 ppm; 5% O_2

ppm NO Final	Time for Oxidation (hours)
200	0.63
40	6.25
10	28.5
1	285.0

3.3.1.2 Oxidation Time for N_2O_3 Absorption

If, on the other hand, it is assumed that N_2O_3 is the absorbing species, then the following equations apply:

$$2NO + O_2 \rightarrow 2NO_2\text{, slow} \qquad (8)$$

$$2NO_2 + 2NO \rightarrow 2N_2O_3\text{, fast} \qquad (9)$$

$$\overline{4NO + O_2 \rightarrow 2N_2O_3} \qquad (10)$$

Equation (8) is the rate controlling step, but the overall stoichiometry is represented by Equation (10). Analysis similar to that previously given results in Equation (11):

$$\frac{1}{P_{NO}} - \frac{1}{(P_{NO})_{In}} + \frac{1}{[4(P_{O_2})_{In}-(P_{NO})_{In}]} \ln \left[\frac{(4P_{O_2})_{In}\ (P_{NO})}{[(P_{NO})_{In}\ (4P_{O_2})_{In}-(P_{NO})_{In}+P_{NO}]} \right]$$

$$= \frac{k}{4} [(4P_{O_2})_{In} - (P_{NO})_{In}]\ t \qquad (11)$$

The oxidation times required to produce the final NO concentrations in Table 3-4 are almost identical in this case to the previous values. This results from the fact that for the conditions under consideration,

$$(P_{O_2})_{In} >> (P_{NO})_{In}$$

so that both Equations (7) and (11) reduce to:

$$\frac{1}{P_{NO}} - \frac{1}{(P_{NO})_{In}} = k(P_{O_2})_{In}\ t \qquad (12)$$

These computed oxidation times are comparable to the recommended "times of standing" for the phenol disulfonic acid method (547,204,425). This correspondence adds further credence to the argument that the oxidation step is rate controlling in the oxidation-absorption process.

It is evident, therefore, that analysis times could be considerably decreased if the oxidation times were reduced. This concept has been described in the literature in connection with instrumental methods of analysis for NO using ozone or dichromate paper for the oxidation (6,10). The ozonization method, however, suffers from problems associated with the production of higher oxides of nitrogen, such as N_2O_5, which may yield erroneous analytical results for gas phase spectrophotometric determination of NO_2. The higher oxides of nitrogen (N_2O_5) should not be a problem, however, if aqueous absorption is used to collect the sample.

A simple and obvious method of reducing the oxidation time is to increase the oxygen partial pressure (see Section 4.3 for further discussion). To illustrate this concept quantitatively, consider addition of a flue gas of the composition previously assumed (NO = 400 ppm, O_2 = 5%) to a sampling vessel containing 0.5 atmosphere of pure oxygen, to a final pressure of one atmosphere. The partial pressures of the components after mixing will be:

$$P_{O_2} = 0.5 + 0.05 \times 0.5 = 0.525 \text{ atm}$$

$$P_{NO} = 0.5 \times \frac{400}{10^6} = 200 \times 10^{-6} \text{ atm}$$

Using these initial values, and substituting into Equation (12), the oxidation times necessary to produce the various final NO concentrations are given in Table 3-5.

TABLE 3-5

COMPUTED OXIDATION TIMES FOR TYPICAL FLUE GAS SAMPLES WITH O_2 ENRICHMENT

Initial (NO) = 400 ppm

ppm NO Final	Time for Oxidation (hours)
40	0.45
10	2.3
1	23

The oxidation times have been reduced by an order of magnitude compared to the previous results in Table 3-4. Thus, this technique may provide a simple but effective means of reducing the time required for analysis.

In summary, based on the premise that NO_2 or N_2O_3 are the only species absorbed into solution, it has been shown that the times required to oxidize 97% of the NO in the sample are of the order of 30 hours (for a flue gas containing 400 ppm NO and 5% O_2). This value compares well with the recommended "standing time" presently utilized in the PDS method (Section 4.3.1). The oxidation is, therefore, probably the rate controlling step in the oxidation-absorption process and may be considerably speeded up by increasing the oxygen partial pressure or by addition of other oxidants, such as ozone.

3.3.2 Absorption Rates of the Oxides of Nitrogen in Aqueous Solution

Wendel and Pigford (572), writing on the kinetics of nitrogen tetroxide absorption in water, state: "Despite the large quantities of nitric acid made by the absorption of nitrogen oxides in water, the kinetics and reactions involved are not yet fully explained ..." A simple reason for the confusion that still exists in the analysis of the absorption is the large number of possible reactions that can occur in the liquid absorbent and the complex interaction between these reactions and the transport processes.

The absorption of equilibrium mixtures of NO_2, N_2O_4 in N_2 (or air) into aqueous solutions has been extensively studied usually in wetted wall columns. The results obtained in long wetted wall columns by Bolshakoff (577) and Chambers and Sherwood (573) indicate that gas-film resistance controls the absorption of nitrogen dioxide into aqueous solutions of nitric acid and sodium hydroxide.

On the other hand, there is some evidence that the absorption rate may be controlled by a chemical reaction occurring in the liquid phase and/or possibly the gas phase. Eagleton, Langer and Pigford (574) reported that the slow rate of reaction between dissolved nitrogen dioxide and liquid water limited the rate of nitrogen dioxide absorption into strong caustic solutions in long wetted wall columns. Peters and Holman (578), also working with long wetted wall columns, concluded that both the gas and liquid phase reactions between N_2O_4 and water controlled the absorption. Peters, Ross and Klein (579) using a bubble cap plate column for absorption studies indicate that the gas phase reaction is the controlling one. However, Denbigh and co-workers (580,581) using short wetted wall columns, have reported that the rate of absorption of nitrogen dioxide into aqueous solutions was determined by the reaction of nitrogen tetroxide with water, was proportional to the N_2O_4 concentration in the gas phase and was not diffusion controlled.

The existence of the gas phase homogeneous reaction between NO_2-N_2O_4 and water is an unsettled question which follows from the controversial evidence discussed above. The evidence in favor of the gas phase reaction results mainly from the absorption of NO_2-N_2O_4 in alkaline solutions (573,574) in which nitric oxide and mist was observed in the off gases. Since sodium nitrite does not decompose in alkaline solution, it is postulated that NO_2 must have reacted with water vapor in the gas phase, producing NO and acid mist. On the other hand, the absence of mist and NO in many similar experiments (580,581) has been cited as opposing evidence.

The presence of nitric oxide in the NO_2-N_2O_4 absorbing gas mixture complicates analysis of the absorption rates and mechanism. Eagleton, Langer and Pigford (574) were the first to report that the presence of NO in the feed gas stream to a wetted wall tower, using 46% NaOH solution as the absorbing medium, resulted in absorption rates as much as ten times faster than those reported for NO_2 absorption in a similar experiment. Recently, Peters and Koval (582) have suggested that nitric oxide influences the rate of reaction of NO_2 with water even when NO is not present in the inlet gas stream. Koval and Peters (583) attempted to discern the effect of NO addition on NO_2 absorption in aqueous solution in a wetted wall column, and concluded that a critical factor in analyzing absorption data, particularly from a short residence time contactor, is the nitrous acid concentration.

The principal reactions which control the absorption of nitrogen oxides in aqueous solution are:

$$2NO_2(g) \rightleftharpoons N_2O_4(g) \tag{13}$$

$$NO(g) + NO_2(g) \rightleftharpoons N_2O_3(g) \tag{14}$$

$$2NO_2(g) \text{ or } N_2O_4(g) \rightleftharpoons 2NO_2(aq) \text{ or } N_2O_4(aq) \tag{15}$$

$$N_2O_3(g) \rightleftharpoons N_2O_3(aq) \tag{16}$$

$$2NO_2(aq) \text{ or } N_2O_4(aq) + H_2O \rightleftharpoons HNO_3 + HNO_2 \tag{17}$$

$$N_2O_3(aq) + H_2O \rightleftharpoons 2HNO_2 \qquad (18)$$

$$3HNO_2 \rightleftharpoons HNO_3 + 2NO + H_2O \qquad (19)$$

Reactions (13) and (14) occur in the gas phase, are extremely rapid and are generally assumed to be in equilibrium; Reactions (15) and (16) are physical equilibria; Reactions (17), (18), and (19) represent the liquid phase reactions. In most studies, up to two of the latter three reactions (17-19) are assumed to be in equilibrium; the remaining reaction(s) control the rate of absorption. The selection of reactions in equilibrium depends on the ratio of the overall time for reaction to the half life of the reaction. The difference in reported results on nitrogen oxide absorption may frequently be explained by the number of reactions (17-19) assumed to be in equilibrium; i.e., the overall reaction (or absorption) time has a major effect.

The overall chemical reaction may be represented by:

$$3NO_2(g) + H_2O \rightleftharpoons 2HNO_3 + NO(g) \qquad (20)$$

The equilibrium constant for Reaction (20) is:

$$K_{20} = \frac{P_{NO}\ a^2_{HNO_3}}{P^3_{NO_2}\ a_{H_2O}}$$

where a_{HNO_3} and a_{H_2O} represent the activities of HNO_3 and H_2O in the liquid. For convenience, this expression is usually separated into two parts, the first a function of the equilibrium gas composition, and the second dependent only upon the concentration of HNO_3 in the liquid (Equation 21):

$$K_{20} = K_1K_2 = \frac{P_{NO}}{P^3_{NO_2}} \cdot \frac{a^2_{HNO_3}}{a_{H_2O}} \qquad (21)$$

The product, K_1K_2, can be computed from standard free energy and vapor-pressure data as shown by Wenner (584) and Forsythe and Giaque (585) permitting a plot of $P_{NO}/P^3_{NO_2}$ versus acid concentration to be obtained (Figure 3-5). The equilibrium constant for Reaction (13) has been shown by Wenner (584) to be given by:

$$\log_{10}K_{13} = \frac{2993}{T} - 9.226 \text{ atm}^{-1} \qquad (22)$$

The equilibrium concentration of Reaction (14) can be computed from the data of Verhoek and Daniels (508) although the concentrations of N_2O_3 are in most cases extremely small.

Figure 3-5 and Equation (22) may be employed to calculate the equilibrium concentrations of NO_2 and NO above pure water, for a flue gas containing initially 400 ppm NO which has been oxidized to 400 ppm NO_2 (total pressure 1 atm). Since from Equation (20), moles NO_2 absorbed equals three times moles NO evolved, we have by material balance:

3 (moles NO evolved) = moles NO_2 absorbed

= initial moles NO_2

= (moles NO_2 reacted to N_2O_4 + moles NO_2 remaining) (23)

$$\therefore\ 3P_{NO} = 400 \times 10^{-6} - \left[2P_{N_2O_4} + P_{NO_2}\right] \qquad (24)$$

$$\therefore\ 3K_1(P_{NO_2})^3 = 400 \times 10^{-6} - \left[2K_{13}(P_{NO_2})^2 + P_{NO_2}\right] \qquad (25)$$

where P_{NO_2} = final NO_2 partial pressure, atm

P_{NO} = final NO partial pressure, atm

$P_{N_2O_4}$ = final N_2O_4 partial pressure, atm

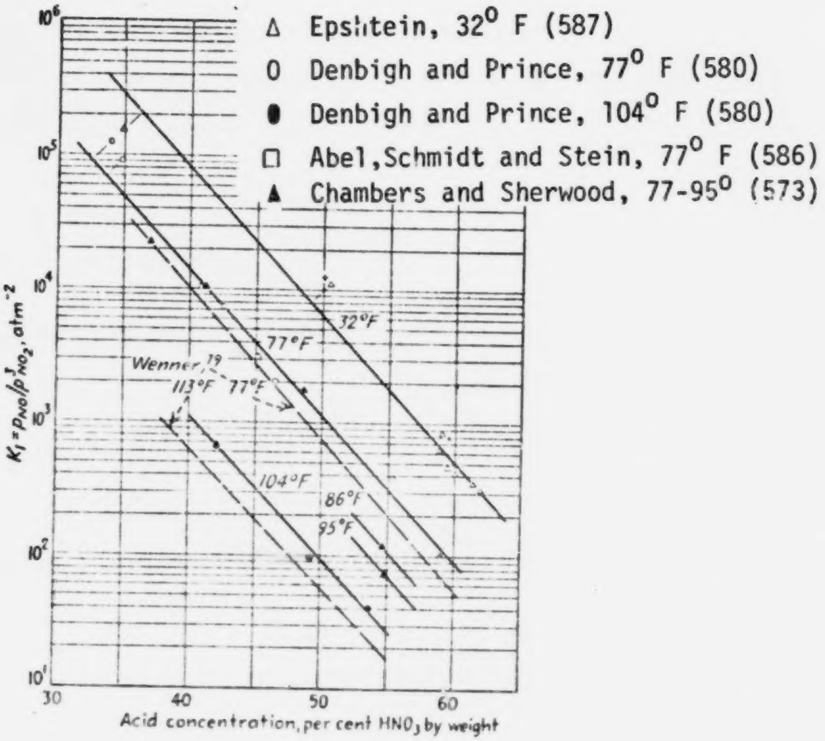


Fig. 3-5 Equilibrium Vapor Pressures of NO_2 and NO over Nitric Acid

Extrapolating Figure 3-5 to 0% HNO_3 gives (at 77°F) $K_1 \simeq 10^8$ atm^{-2}, and from Equation (20), $K_3 = 6.56$ atm^{-1}. Substitution of these constants into Equation (25) and solving by trial and error gives $P_{NO_2} \simeq 10^{-4}$ atm, or a final concentration of $NO_2 \simeq 100$ ppm. This simple example clearly indicates the necessity for an oxidizing reaction to occur in the liquid absorbing media in order to drive Reaction (20) continuously to the right.

Previous discussion of the kinetics of absorption indicated that good correlation of experimental data could be obtained in many situations if the following rate equation is used:

$$\frac{-dc_{NO_2}}{dt} = k\ C_{N_2O_4} \tag{26}$$

The basic assumptions in the theoretical development of Equation (26) were:

(1) The rate of removal of NO_2-N_2O_4 is controlled by Reaction (17).

(2) The chemical reactions occur under irreversible consitions.

(3) Instantaneous equilibrium exists between NO_2 and N_2O_4.

(4) The nitrous acid concentration is negligible or unchanging.

The fourth assumption has major implications for application of the data reported for short contact time absorbers to batch absorption systems (of the type likely to be encountered in analytical systems) since the nitrous acid concentration cannot be considered unchanging as the contact time increases. Indeed, Peters and Koval (582) in studying the absorption of NO_2-N_2O_4 in an agitated reactor (i.e., a reactor of fairly long gas residence time) observed that the effects of N_2O_3 can no longer be ignored because a small fraction of the total oxides was present as N_2O_3, and Reactions (14), (16) and (18) must be included in the analysis. Clearly, where NO is added to the NO_2-N_2O_3 mixture, Reactions (14), (16) and (18) must also be considered. Consequently, these reactions should be considered in absorption processes for the analysis of nitrogen oxides in flue gas which are NO-NO_2 mixtures. However, the equilibrium position for Reaction (14) is such that the N_2O_3 concentrations are exceedingly small for the nitrogen oxide concentrations characteristic of flue gases (obtained as the oxidation proceeds) so that including the effect of N_2O_3 in the analysis of absorption rates is probably not necessary. As a first approximation, in studying the absorption of the nitrogen oxides produced by the oxidation of flue gas nitric oxides, it will, therefore, be assumed that the rate can be described by an equation similar to Equation (26).

The data of Wendel and Pigford (572) for the kinetics of the absorption of N_2O_4 in water are probably some of the best in the literature and compare favorably to the results of Denbigh and Prince (580). Their data can be approximated by the following equation:

$$N_A = 35 \times 10^{-6} P_{N_2O_4} \qquad (27)$$

where N_A = flux of absorbing species in $\frac{\text{gm moles } N_2O_4}{\text{cm}^2 \text{ sec}}$

$P_{N_2O_4}$ = bulk partial pressure N_2O_4, atm

Equation (27) can be used to estimate a typical time for absorption of a gas consisting of 400 ppm NO_2 in an inert matrix (i.e., after the oxidation of NO has been completed). The gas is contained in a volume, V liters, at 1 atm pressure and 25°C; the absorbing surface is A cm^2. Considering the gas space as a system and performing a material balance on N_2O_4 gives, therefore:

$$\frac{dn_{N_2O_4}}{dt} = - 35 \times 10^{-6} A P_{N_2O_4} \qquad (28)$$

where $n_{N_2O_4}$ = moles N_2O_4

$$\therefore \frac{V}{RT} \frac{dp_{N_2O_4}}{dt} = - 35 \times 10^{-6} A\ P_{N_2O_4} \qquad (29)$$

Equation (29) is readily integrated to give:

$$\ln \frac{(P_{N_2O_4})_{Initial}}{(P_{N_2O_4})_{Final}} = 35 \times 10^{-6}\ RT\ \frac{A}{V}\ t \qquad (30)$$

Since it is assumed that NO_2 and N_2O_4 are in equilibrium given by:

$$K_{13} = \frac{P_{N_2O_4}}{P^2_{NO_2}} \qquad (31)$$

Equation (31) can be substituted into Equation (30) to give:

$$2 \ln \frac{(P_{NO_2})_{Initial}}{(P_{NO_2})_{Final}} = 35 \times 10^{-6}\ RT\ \frac{A}{V}\ t \qquad (32)$$

For a typical analytical absorption system we may take: V = 1 liter and A = 100 cm^2. The time to absorb sufficient NO_2 to reduce $(P_{NO_2})_{Final}$ to 10×10^{-6} atm is given by:

$$t = \frac{2 \ln 40}{(35 \times 10^{-6}) \times .082 \times 298 \times 100} = 86 \text{ sec}$$

It must be emphasized that it has been assumed in the material balance, Equation (28), that the gas phase is well mixed, i.e., that no N_2O_4 or NO_2 concentration gradients exist. In actual practice, this will not be the case unless stirrers are placed in the gas space. Furthermore, it is also assumed that the absorbing liquid does not begin to saturate with nitrous and nitric acids, i.e., that the liquid is well mixed and of such a volume that the acid concentrations are negligible. Once again, this is probably not quite correct.

However, it appears on the basis of the above sample calculation that absorption rates are much faster than the oxidation rates, confirming that, as assumed in the previous section, the overall absorption process is probably controlled by the rate of nitric oxide oxidation.

3.3.3 Experimental Studies on Oxidation Times for NO

In order to verify the hypothesis that the gas phase oxidation of NO is the rate determining step in the absorption of nitrogen oxides in aqueous solutions (Section 3.3.1), some preliminary laboratory work was conducted. Tests were run in a gas-fired combustion effluent doped to higher NO_x levels with NO. The results are given in Table 3-6 below. See also Section 5.3.2 for additional studies using caustic absorption.

TABLE 3-6

COMPARISON OF MEASURED AND CALCULATED NO_x LEVELS

Sample No.	Absorption Time (hr)	ppm NO_x (nitrate electrode)	ppm NO_x (calculated)	ppm NO added
1	0.5	293	287	447
2	>24	438	---	447
3	1	1028	1066	1174
4	>24	1160	---	1174

The calculated NO_x values were derived from Equation (12) using the measured oxygen content in the flue of 9%. The agreement between the calculated and measured NO_x values for runs 1 and 3 is excellent. The details of the nitrate electrode method are given by Driscoll, et al. (619). Thus, we see that the rate determining step in the absorption of the nitrogen oxides is presumably the gas phase oxidation of nitric oxide. This indicates that substantial savings in analysis time can be made by using the technique of oxygen enrichment described in Section 3.3.2 with the PDS or other methods for NO_x analysis.

4. METHODS FOR DETERMINATION OF TOTAL OXIDES OF NITROGEN

4.1 Introduction

Flue gases contain nitric oxide and a small but poorly defined fraction of nitrogen dioxide. Manual methods for collection and analysis of total oxides of nitrogen depend upon a number of reaction steps schematically shown below:

$$\left.\begin{matrix} NO \\ + \\ NO_2 \end{matrix}\right\} \xrightarrow{\text{oxidation}} \left.\begin{matrix} NO_2 \\ N_2O_3 \\ N_2O_5 \end{matrix}\right\} \xrightarrow[\text{hydrolysis}]{\text{aqueous absorption}} \begin{matrix} \xrightarrow{\text{Saltzmann reagent}} \\ \xrightarrow[H_2O_2 \text{ or } KMnO_4]{} \end{matrix} \begin{matrix} \text{analysis for } NO_2^- \\ \text{and/or} \\ \text{analysis for } NO_3^- \end{matrix}$$

Since there are no "good" specific wet chemical methods for nitric oxide, oxidation is a required step. The most commonly used oxidizing agent for this reaction is molecular oxygen. Ozone has also been used for oxidation prior to (continuous) gas phase spectrophotometric readout. The oxidation methods in current use are described in detail in the following section on sampling and analysis methods for total NO_x.

After oxidation of nitric oxide, the (higher) nitrogen oxides may be collected by absorption in aqueous solutions. If Saltzmann or other Griess-type coupling reagent is used as the collection medium, the nitrite determined may be used as a measure of the total nitrogen oxides concentration. An oxidizing agent such as hydrogen peroxide or potassium permanganate may be utilized in the absorbing solution to oxidize nitrite to nitrate for determination of total oxides of nitrogen as nitrate. The following sections, therefore, include discussion of measurement techniques for both nitrate and nitrite.

Since we cannot separate sampling and analysis methods completely (for realistic field methods), we have divided total NO_x methods into the following classes:

(a) Those which have been used in effluents (power plant, auto and diesel exhausts or nitric acid plant effluents); these methods include sampling as well as analysis.

(b) Methods which have been used mainly for measurement of nitrate in aqueous solutions or nitrite (NO_2) in ambient air.

Methods for determination of the individual oxides, NO or NO_2, present completely different problems and are discussed subsequently.

4.2 Sampling

4.2.1 General

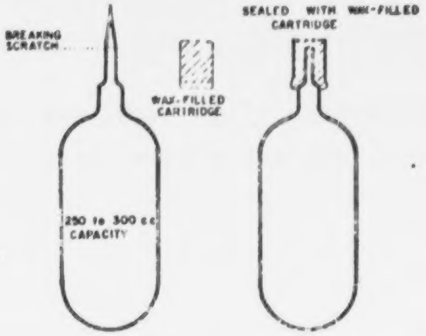
Sulfur oxides are ordinarily collected by methods which concentrate the sample, e.g., absorption in a liquid. This procedure is a feasible one as a result of the relatively high solubility of sulfur oxides in aqueous media. The solubilities of a number of common gases encountered in flue gas sampling are given in Table 4-1 (525).

TABLE 4-1

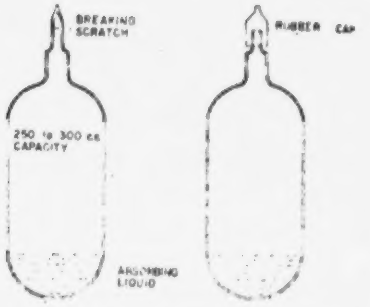
SOLUBILITIES OF COMMON GASES IN WATER AT 20°C

Gas	Solubility, g/l of Water
Nitrogen	0.010
Oxygen	0.044
Nitric oxide	0.063
Carbon dioxide	1.74
Hydrogen sulfide	3.98
Sulfur dioxide	117

The solubility of nitric oxide in distilled water is comparable to that of the common permanent gases, N_2 and O_2. The solubility of SO_2 is, however, more than three orders of magnitude greater than that of NO. Since high solubility is a prerequisite for quantitative collection by scrubber devices, the techniques used for nitrogen oxides have been limited to grab samplers which function by mechanical retention followed by absorption (Figures 4-1 and 4-2). Power plant sampling has ordinarily been conducted by collection in evacuated flasks, although plastic bags have been widely used in automotive studies.

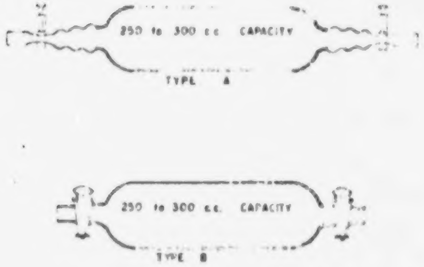

BREAKING SCRATCH
WAX-FILLED CARTRIDGE
SEALED WITH WAX-FILLED CARTRIDGE
250 to 300 cc CAPACITY

Evacuated Sample Container.


BREAKING SCRATCH
RUBBER CAP
250 to 300 cc CAPACITY
ABSORBING LIQUID

Evacuated Sample Container for Collection of Sample in an Absorbent.

Reproduced from best available copy.


250 to 300 cc CAPACITY
TYPE A
250 to 300 cc CAPACITY
TYPE B

Gas Sample Tubes for Collection of Sample by Displacement.

Figure 4-1. Types of Grab Samplers (partial).

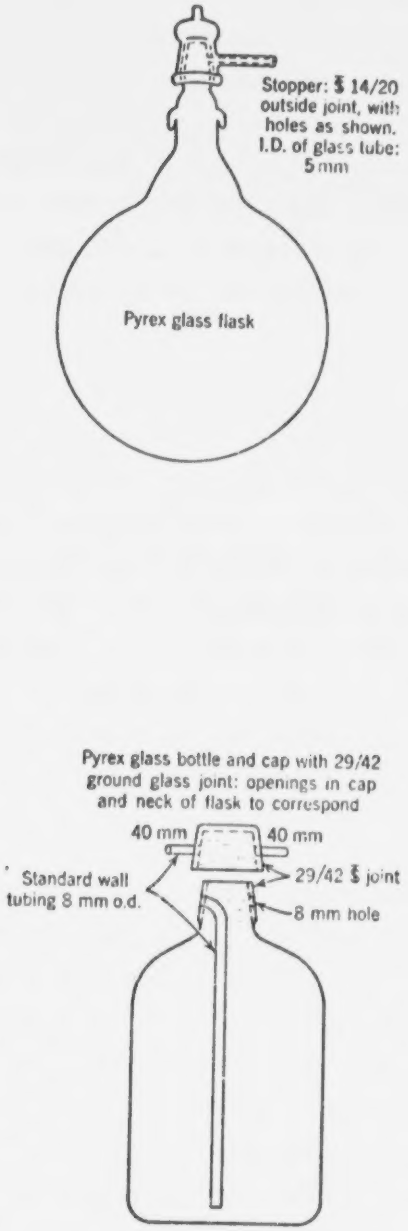

Stopper: $ 14/20 outside joint, with holes as shown. I.D. of glass tube: 5 mm
Pyrex glass flask
Pyrex glass bottle and cap with 29/42 ground glass joint: openings in cap and neck of flask to correspond
40 mm
40 mm
Standard wall tubing 8 mm o.d.
29/42 $ joint
8 mm hole

Figure 4-2. Additional Grab Samplers (507).

The selection of a probe for collection of total oxides of nitrogen from a flue is not as difficult a problem as that for sulfur oxides sampling. For the latter, losses due to condensation of H_2SO_4 and dissolution of SO_2 and SO_3 in condensate water must be prevented. Temperature controlled probes are, therefore, employed for the quantitative collection of SO_x. The very low solubility of the principal oxide of nitrogen, NO, considerably reduces the magnitude of this problem in sampling for total NO_x. Simple stainless steel or pyrex tube is generally adequate for the sampling probe. A complete NO_x sampling train is illustrated in Figure 4-3 (173).

4.2.2 Integrated Grab Sampling

A major difficulty in the interpretation of conventional grab samples results from the short sampling time (seconds to minutes). There is a significant advantage in collection of a sample integrated over a full operational cycle characteristic of the equipment under test; this is the direct relationship between the integrated sample and the average emission, which is ordinarily the objective of the measurement. Of course, a number of grab samples may be averaged to obtain the integrated emission during a cycle, but this is clearly a more tedious approach.

An integrated grab sample may be obtained by inclusion of a critical orifice in the sampling line as shown in Figure 4-3. Critical orifices are available for flow rates as low as 25 ml/min (507) but the small diameter of the orifice required for the lowest flow rates may lead to erratic flow control as a result of plugging by particulates even when a prefilter is installed. Brief and Drinker (260), for example, have reported repeated plugging during stack sampling using an orifice sized for flow of 25 ml/min. A 100 ml/min orifice may represent a reasonable compromise. Such an orifice used with a 5-liter evacuated flask will provide 25 min sampling time (since critical flow will continue only up to flask pressures below 0.5 atmosphere). This technique would provide considerable improvement over present grab sampling methods which usually have integration times as short as seconds.

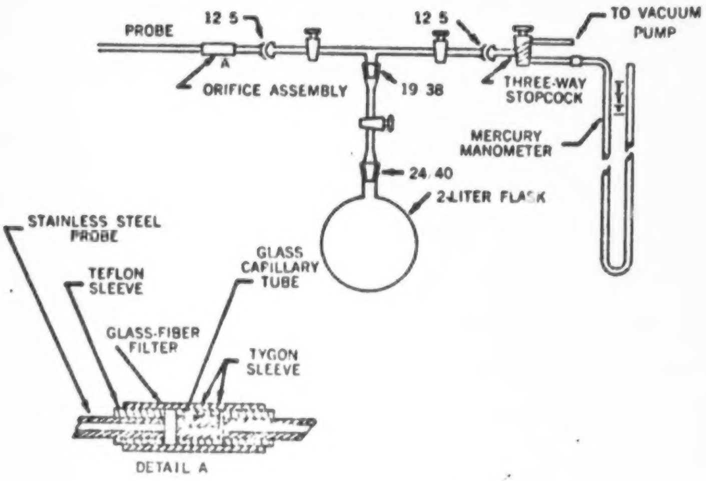

PROBE
12 5
12 5
TO VACUUM PUMP
A
ORIFICE ASSEMBLY
19 38
THREE-WAY STOPCOCK
MERCURY MANOMETER
24/40
2-LITER FLASK
STAINLESS STEEL PROBE
TEFLON SLEEVE
GLASS CAPILLARY TUBE
GLASS-FIBER FILTER
TYGON SLEEVE
DETAIL A

Figure 4-3. Apparatus for integrated grab samples- PHS NO_x sampling train (173)

It is of interest to note that Brief and Drinker employed a partially opened stopcock as a simple critical orifice (260). They observed that sonic velocity is maintained up to flask pressure of 0.4 atm.

4.3 Sampling and Analysis Methods Used for Total NO_x Determinations in Exhaust Gases

4.3.1 Phenol Disulfonic Acid (PDS) Method (1,9,76,77,134,278, 388,404,428,433,425,512,536,547)

4.3.1.1 Description

An aqueous sample containing nitrate (from absorption of nitrogen oxides in 0.1N H_2SO_4/H_2O_2) is made slightly alkaline and evaporated to dryness. The solids are dissolved in PDS reagent (30% PDS in concentrated H_2SO_4) to give nitrophenol-disulfonic acid. When made sufficiently alkaline (generally with NH_4OH), the nitro compound has a yellow color (absorption maximum = 410 nm); the optical density is proportional to the amount of nitrate in the original sample.

Some standard procedures (134,404) recommend diluting the PDS sample mixture to 70% H_2SO_4 and heating for a few minutes before the final dilution and addition of base; however, none of the cited references give justification for this step.

The final concentration of NH_4OH (in excess of that to neutralize the H_2SO_4) in the solution varies from 0.3 molar (278) to 0.75 molar (76,77,428) to 3 molar (404), the higher concentrations having a higher pH; use of KOH in place of NH_4OH gives a higher pH, and 5 to 10% more intense color (428,433).

4.3.1.2 Application

This is the most widely used method for measuring NO_x (absorbed into dilute H_2SO_4/H_2O_2) in flue gases (1,134,404,547,76,137, 425,512,347,204,536). It has also been used for automotive (7) and diesel exhausts (9). The method is also widely used for nitrate in agricultural material, soil and water.

4.3.1.3 Sampling

Nitrogen oxides in power plants are collected by taking grab samples in 1- or 2-liter evacuated flasks. The most common absorbent is acidic (0.06N H_2SO_4) peroxide (7,76,137,404,425,512,347,204, 536). The peroxide serves a two-fold purpose: oxidation of NO_2^- to NO_3^- and $SO_3^=$ to $SO_4^=$. For flue gas samples which contain 3 to 5% oxygen, overnight contact time is generally employed (7,137,76,404). Gill (77) and Beaty, et al. (209) use a 2 to 3 hour contact time. However, their work is with ambient air samples and/or tunnel atmospheres where the oxygen content is generally 3 to 4 times higher than in combustion sources. The low oxygen concentration in fossil fuel combustion would account for the longer absorption time required since the gas phase oxidation of NO is the limiting step.

In the early work on the PDS method for air analysis, alkaline peroxide absorbing solutions were used. These were discontinued when Francis and Parsons (453) found low results. They attributed this to incomplete oxidation of nitrite in caustic solution as a result of low reaction rate. Since nitrite gives nearly the same response to PDS as nitrate, the actual reason is not known.

An alternative to the acidic peroxide absorbent is acid permanganate which has been used by API (204). This method offers no apparent advantage over peroxide. On the basis of limited data (204), the precision is somewhat poorer than for peroxide absorbent.

4.3.1.4 Applicable Concentration Range

The absorbance-concentration curve generally covers the range of 0-100 ppm NO_2 (134,404). The method is generally employed for measuring from a few ppm to a few thousand ppm NO_x (76,77,134, 404), the upper limit being extended by appropriate aliquoting or dilution. The upper range can also be extended by measuring the absorbance at 500 nm.

4.3.1.5 Precision and Accuracy

See Section 6 for precision and accuracy data on the PDS method.

4.3.1.6 Interferences

Halides cause variable losses, particularly at low NO_x levels. Br^- equivalent to 2.5 ppm HBr added to NO_3^- equivalent to 40 ppm NO_2 resulted in a 5% loss in NO_2 (7). For a solution of NO_3^- equivalent to 400 ppm NO_2, addition of Cl^- equivalent to 16 ppm HCl caused 2 to 8% loss, and Cl^- equivalent to 48 ppm HCl resulted in 13 to 17% loss (433). The halogen (approximately 25 ppm) expected from gasoline in automotive exhaust gases will cause less than 2% loss in apparent NO_x (assumed 1200 ppm NO_x) by the PDS method (7).

Nitrite gives an interference equivalent to 80% of the nitrate response with the PDS method (see Section 5.3.2). Excess halides can be removed by adding slightly less than the stoichiometric amount of Ag_2SO_4 and filtering off the AgCl before evaporating the sample (278,433).

The effect of SO_2 on NO_x determinations by the PDS method has been checked by NAPCA (548). They find no decrease in apparent NO_x concentrations even when the SO_2 is present in a ten-fold excess (2000 ppm). (See Figure 4-4.)

With the strong H_2SO_4, unburned hydrocarbons may give colored products which will interfere with the photometry (323). This problem should not be serious, however, in large power plants which are operated with close control of combustion conditions.

4.3.1.7 Comments

This method is the one most widely used in the United States for measuring nitrate in aqueous solution. The method was developed by Chamot, et al. (433) around 1910, and adapted to give a working method for nitrogen in air (including sampling) by Beatty, Berger and Schrenk in 1943 (428).

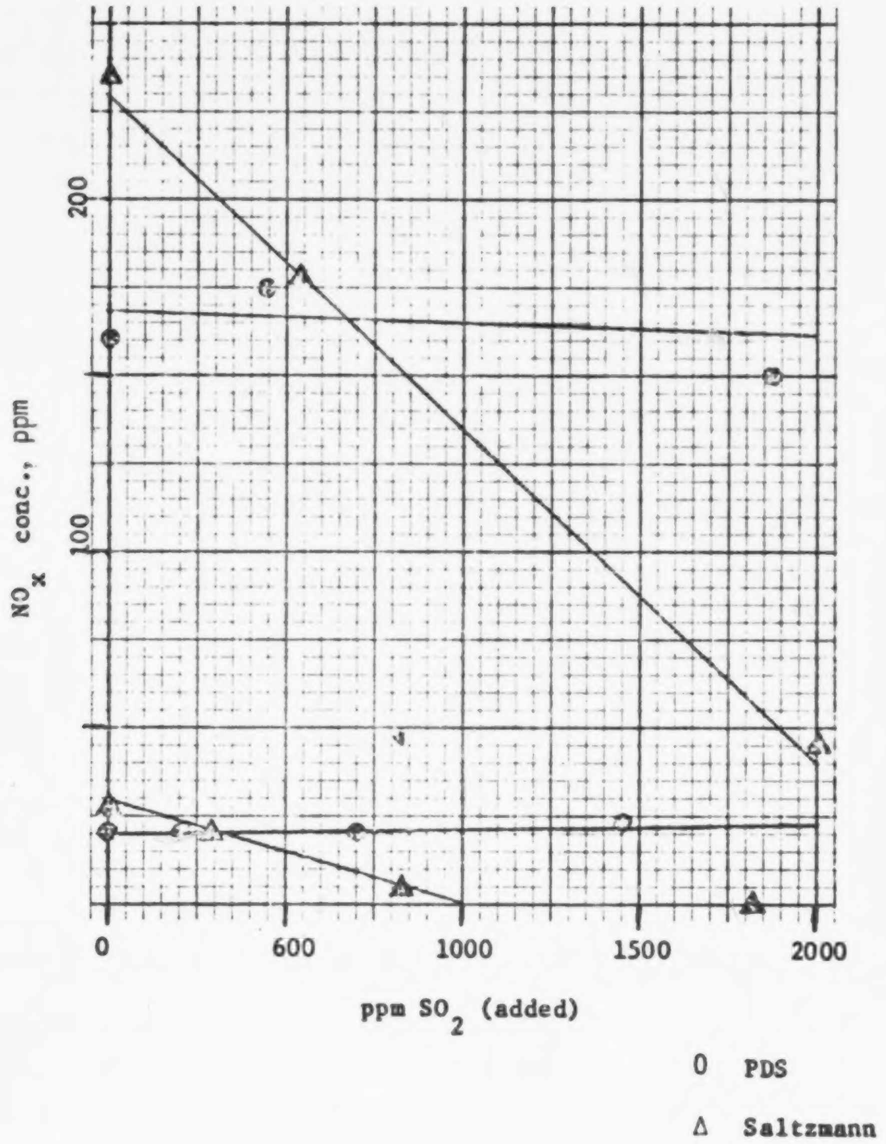


Figure 4-4 Effect of SO_2 concentration on apparent NO_x concentration by PDS and Saltzmann methods (548)

Beatty, et al. (428) used 0.1N H_2SO_4 plus 0.1% H_2O_2 as the absorbing solution. More recent versions of this method have employed H_2O_2 concentrations of from 0.06% to 0.4% (134,404,76). The peroxide serves a two-fold purpose, both to oxidize any nitrate and to convert sulfite, an interference, to sulfate.

After absorption, the solution is made alkaline with potassium or sodium hydroxide and slowly evaporated to dryness to avoid spattering losses. This evaporation step is time-consuming and generally requires from a few hours to overnight depending on the amount of solution and the equipment. Obviously, minimizing the solution volume would decrease the evaporation time.

The PDS reagent is composed of 25 g of phenol in 150 ml of concentrated H_2SO_4 + 75 ml 15% fuming H_2SO_4. Two ml of this reagent is sufficient to wet and dissolve the solids from the absorbant solution since this amount of reagent has been shown to react with 1.2 mg NO_2 (equivalent to 600 ppm in a liter) (77).

Virtually, all procedures allow a 2-minute nitration reaction time. This was originally established by Chamot (433) and checked by Gill (77) on samples containing up to 1.2 mg NO_2. In fact, Gill found 96% recovery for 1.2 mg NO_2.

Some standard procedures (134,404) call for addition of 1 ml of H_2O and four drops of concentrated H_2SO_4 and warming for 3 minutes after the nitration is completed. No reason is cited for this operation (although it is probably included to help dissolve all the solids), and it was not deemed necessary by the developers of the method.

The yellow color produced on making the solution alkaline is due to the ionization of the phenolic proton from the 6-nitrophenol-2,4-disulfonate (433). Since this species is a weak acid (pK of o-nitrophenol = 7.2, pK of phenol-p-sulfonate = 9.0), the final solution must either be sufficiently alkaline so that complete ionization takes place, or be very reproducibly buffered. Thus, the nitrate calibration solutions must be run exactly as the samples, so that the same volumes of reagents are used.

NH_4OH is recommended as the base in most procedures and is useful for avoiding precipitation of silver oxide when silver salts are used to remove halogen. KOH does give some 5 to 8% more color intensity (428,433) presumably because of the higher pH of the final solution.

The sampling technique described by Dimitriades (7) provides more precise results than the conventional PDS grab sampling techniques (see Section 6.3). He collects a dried, proportional sample of the exhaust in a 50-liter plastic bag. The replicate grab samples are then taken from the plastic bag. This procedure minimizes sampling errors and smooths source fluctuations. If the residence times in the bag are too long, the accuracy may be of some question because of absorption of NO_2 on the walls.

4.3.1.8 Conclusions

The advantages include wide concentration range, minimum number of sample handling steps, and no interference from the SO_2 in flue gases. The disadvantages are the long elapsed time* and a possible interference from halides. It may be possible, however, to shorten the long elapsed time by addition of oxygen or ozone in the flask after the oxides of nitrogen are collected (Section 3). The sampling technique used by Dimitriades may provide increased precision for the PDS method. The accuracy of this sampling method should be checked, however. The PDS method would be more useful if: (1) elapsed time could be shortened (see footnote), (2) if halide interferences could be more easily removed.

4.3.2 Xylenol Isomer Methods

2,4-xylenol (189,323,379); 3,4-xylenol (279);2,6-xylenol (379).

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*Coulehan and Lang (620) have recently modified the PDS method to eliminate the time-consuming step of evaporation to dryness. This had been done by minimization of the volume of the absorbing solution and running the nitration in 50% H_2SO_4. They obtain good agreement between conventional PDS and their modified version of PDS.

4.3.2.1 Description

Aqueous nitrate is mixed with the xylenol and H_2SO_4 to give an acid concentration of from 50% (2,6-xylenol) to 80% (3,4-xylenol), and allowed to react (with or without heating) for approximately 30 minutes. The sample is then diluted with water and steam-distilled into dilute NaOH. The yellow-orange color produced is measured with a spectrophotometer in the 420-440 nm region.

The steam-distillation step can be replaced by extracting the nitroxylenol into toluene and back-extraction into dilute NaOH for measurement (323).

The 2,6-isomer is measured directly in the nitration mixture by UV spectrophotometry (320-330 nm region).

4.3.2.2 Areas of Application

Nitrous fumes in air (189); nitrogen oxides in diesel exhaust (379),* nitrate in water (397).

4.3.2.3 Sampling

In the 2,4-xylenol method (379), the oxides of nitrogen are collected in an evacuated sampling bottle (250 ml) containing 10 ml of 0.05N NaOH solution. To collect the sample, the evacuated flask is inverted and the sample of flue gas is bubbled through the sodium hydroxide solution. After the NO is oxidized and absorbed (3 minutes),† potassium permanganate is added to oxidize nitrite to nitrate. The sample is then analyzed for nitrate by the 2,4-xylenol method.

4.3.2.4 Applicable Concentration Range

2,4-xylenol: 50 to 1000 ppm NO_2 in 1 liter of diesel exhaust (379); also from 4 to 1000 ppm by DuBuboscq (visual) colorimetry (189).

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*BSI states that this method should be suitable for flue gas. It is not, however, apparent that such tests have actually been conducted.

†This short oxidation time is not consistent with kinetic data available. (See Section 3.)

3,4-xylenol: up to 1.1 mg NO_2 (equivalent to 550 ppm NO_2 per liter) (279).

2,6-xylenol: up to 65 μg NO_2 (equivalent to 30 ppm NO_2 per liter) (397). Upper limits can be extended by aliquoting sample.

4.3.2.5 Precision and Accuracy

2,4-xylenol: relative precision is about 5%, no data (379).

3,4-xylenol: coefficient of variation (C.V.) = 1 to 2% from data summary (279).

2,6-xylenol: C.V. = 0.5 to 2%, data summary (397).

No accuracy data found.

4.3.2.6 Interferences

Chlorides - For 2,4-xylenol, 0.4 mg HCl (equivalent to 270 ppm HCl in 1 liter flue gas) caused an apparent decrease of 5 ppm NO_2 at the 34 ppm level (323), while 500 ppm HCl was reported to give a negative error of less than 5% in the measurement of from 20 to 400 ppm NO_2 in flue gas (379). With 2,6-xylenol, chloride causes a small, positive error; the equivalent of 600 ppm HCl causes only a 3% error at the 40 ppm NO_2 level.

Nitrites - Interference by formation of colored products with xylenols (279) and formation of nitrosoxylenols (397).

Oxidants - Give colored products with 2,4-xylenol which are co-distilled with nitroxylenol (279,323). Traces of $KMnO_4$ apparently do not interfere (189,379).

Organics - Up to 20 mg of sucrose (added as a model compound) gave losses equivalent to only 1 ppm NO_2 (323). Organics which are found in ground water result in negative errors with 2,6-xylenol (397).

4.3.2.7 Comments

(a) Steam distillation is a tedious step. The double extraction into toluene and back into aqueous NaOH (323) may be useful, but this is still a problem due to emulsion formation.

(b) Losses of nitro compound from volatilization can occur if the temperature rises more than 40°C during addition of acid or subsequent nitration period.

(c) Oxidants, except for traces of $KMnO_4$, must be destroyed.

(d) Sensitivity and acidity requirements are such that the sample (or an aliquot) can be run directly without the evaporation step.

4.3.2.8 Conclusions

The lower acidity required for nitration is one advantage over PDS since it is not necessary to evaporate the sample. Xylenols are quite sensitive to oxidants, and require a separation step before measurement. Although the total elapsed time is shorter for xylenols, there are more sample handling steps than with PDS. In view of this, the xylenol procedures offer no outstanding advantage over the PDS method.

4.3.3 Iron (II) Sulfate (and Other Complexes)

4.3.3.1 Description of Method

The nitrogen oxides in the gas are absorbed in 75% H_2SO_4, then iron (II) sulfate in 75% H_2SO_4 is added. Nitric oxide reacts with ferrous sulfate to produce ferrous nitrosyl sulfate. This complex absorbs strongly in the visible region and after 5 minutes is measured spectrophotometrically at 520 nm. The color is stable for 2 hours. The reactions with the oxides of nitrogen are:

$$FeSO_4 + NO \rightarrow FeSO_4 \cdot NO$$

$$3FeSO_4 + NO_2 + H_2SO_4 \rightarrow FeSO_4 \cdot NO + Fe_2(SO_4)_3 + H_2O$$

4.3.3.2 Areas of Application

NO and NO_2 mixtures in air, and in real and synthetic mixtures of gases from detonation of explosives (5), automotive exhausts (455).

4.3.3.3 Sampling

Samples collected in bubblers at a rate of 0.5 l/min for 5 minutes (455); evacuated flasks containing 75% H_2SO_4 (5).

4.3.3.4 Applicable Concentration Range

50 to 10,000 ppm NO_2 with an 800 ml gas sample; sensitivity could be increased by increasing the sample size (5).

4.3.3.5 Precision and Accuracy

Coefficient of variation, 1 to 2% in analysis of gas mixtures containing from 125 to 10,000 ppm of NO. Using $NaNO_3$ solutions for calibration, recoveries of NO and NO_2 added in separate runs were 97% and 90%, respectively (5).

4.3.3.6 Interferences

Nitrate gives identical response; 400 ppm H_2S interferes but 6000 ppm SO_2 did not (5). One possible interference is due to the oxidation of ferrous sulfate by molecular oxygen followed by reaction of the corresponding ferric sulfate with NO. The ferric sulfate does not absorb and, therefore, would produce a negative interference.

4.3.3.7 Comments

Other inorganic salts which absorb nitric oxide are (487):

(a) ferric chloride to produce ferric nitrosyl hexachloride $2(FeCl_3)NO$

(b) ferrous selenate to produce ferrous nitrosyl selenate

(c) potassium nitrosyl disulfonate (454)

Some preliminary work at NAPCA (548) indicates that Fremy's salt (nitrosyl disulfonate) might prove useful for collecting nitric oxide. This is based on the following reaction:

$$\begin{tikzcd}
(KSO_3)_2NO + NO \arrow[r] & (KSO_3)_2NO\text{-}NO \arrow[d, "H_2O"] \\
 & (KSO_3)_2NOH + HNO_2
\end{tikzcd}$$

In basic solution, the salt is highly colored (absorption maximum 540 nm). When NO is bubbled through the solution, bleaching occurs. Collection was evaluated by scrubbing NO (in N_2) with bubblers containing alkaline solutions of Fremy's salt. There were several problems associated with the technique:

(1) What is exact stoichiometry?

(2) Absorbance of bleached solution changed with time indicating a slow reaction of NO in the scrubbing solution.

The latter problem could be solved by taking a grab or integrated grab sample. The former problem would involve additional laboratory work to clear up. To use this method in sources which contain oxidizable components (e.g., SO_2 in large amounts), a prescrubber such as peroxide solution would have to be used.

4.3.3.8 Conclusions

These methods may lead to poorer accuracy than the nitration methods (PDS, etc.), but they may, indeed, prove useful as a fast readout at "high" NO_x concentrations. The method should be considered for a "simplified" method for NO_x in power plants.

4.3.4 Spectrophotometric Determination of NO_2 in the Gas Phase

4.3.4.1 Description

Automotive exhaust samples containing NO are oxidized to NO_2 by solid (dichromate paper) or gaseous oxidizing agents such as oxygen or ozone. The NO_2 formed is then determined spectrophotometrically (at ∿ 400 nm) by optical density measurements in the gas phase (6,7,10,458).

4.3.4.2 Areas of Application

Automotive exhausts.

4.3.4.3 Sampling Equipment

The oxides of nitrogen are collected by grab sampling techniques using evacuated flasks (10) or syringes (458). Methods which employ ozone or dichromate paper (for rapid oxidation of NO) achieved a continuous readout of the absorbance of NO_2 and, therefore, the NO_x concentration.

4.3.4.4 Applicable Concentration Range

10-2000 ppm and up (6,10).

4.3.4.5 Precision and Accuracy

Depends on oxidation step.

4.3.4.6 Interferences

Hydrocarbons and water vapor. SO_2 would be the major problem with gas phase spectrophotometry of NO_2 from power plant effluents since SO_2 is present at high concentrations and reacts with NO_2 in the gas phase (452) to produce SO_3 and NO.

4.3.4.7 Comments

(a) Solid oxidants. Solid $K_2Cr_2O_7$ supported on glass fiber paper (10) was used to oxidize nitric oxide from an auto exhaust and, therefore, determine NO_2 continuously. Ripley, et al. (10) found that 200 ppm of NO could be oxidized quantitatively but at 1000 ppm the efficiency was only 85%. The dichromate paper lost efficiency at a relative humidity higher than 75% or when low concentrations of aromatic hydrocarbons such as toluene were present (91). Dichromate has been used successfully by Wilson and Koplinski (91) for ambient NO_x concentrations as a replacement for the irreproducible permanganate bubbler.

(b) Ozone. Ozone has been used as an oxidizing agent for NO by Singh, et al. (6) and DuPont Instruments (457). DuPont found that, although the oxidation of NO was complete within minutes, not all the NO was converted to NO_2. A substantial portion (30%) was converted to higher oxides (N_2O_5) which do not absorb in the same spectral region as NO_2. Singh, et al. (6) found that the ozone method was in agreement (5%) with PDS analysis for NO_x only for an O_3/NO ratio of 0.5. At higher ratios, low results are obtained, presumably as a result of the oxidation to N_2O_5. At ratios below 0.5, the oxidation was incomplete and results were again low. This dependence of NO_x concentration on the ozone concentration leaves much to be desired if gas phase spectrophotometry is used for NO_2 readout. If the higher oxides of nitrogen were collected in aqueous solutions for NO_3^- analysis, this would not be important in ozone oxidation.

(c) Oxygen. Dried auto exhaust gas is passed into a 50-liter tedlar bag (7). A sample is transferred into an evacuated stainless steel tank until a final pressure of one atmosphere is reached. Then an equal volume of oxygen is added to this mixture to oxidize the nitric oxide to NO_2. A modification of this procedure by the Bureau of

Mines involves prior removal of hydrocarbons by absorption on a heated Hopcalite column. After 45 to 60 minutes, the absorbance of NO_2 is measured with a spectrophotometer (7).

The Chevron research method (458) involves sampling the dried exhaust gas with a 200 cc syringe. The syringe is charged with a 50 cc sample of the exhaust and 100 cc of oxygen. It is then injected into a 113 cc spectrophotometer cell and the absorbance measurement is made when the NO_2 concentration ceases to rise. Although this method is not as rapid as ozone oxidation, less than one hour is usually required. Although the oxygen content of the automotive exhaust gases is low (5%), the presence of hydrocarbons speed up this oxidation process (456). Dimitriades has found that the NO_x values where hydrocarbons ($\sim$ 400 ppm) are removed, are about ten percent higher. The high hydrocarbon content is generally not a problem, however, in gas- or oil-fired power plants but this may be a problem to be considered for the coal-fired plants. The hydrocarbon content for an intermediate-size plant may approach 400 ppm but is generally below this value (see Final Report, Volume I).

A comparison of the above three spectrophotometric methods with the PDS method is given in Table 4-2 [from Dimitriades (7)].

4.3.4.8 Conclusions

Ozone and dichromate paper appear to be interesting oxidants since they permit immediate readout of the NO_x concentrations. The ozone technique is limited in gas phase spectrophotometry because of the formation of higher oxides which do not absorb in the same spectral region. It may, however, be used for continuous NO_x measurement if the NO_2 and higher oxides are collected in an aqueous solution. This technique (continuous determination of NO_x) is not in the mission of the present program. However, addition of ozone to grab samples to decrease the oxidation time is a possible approach. The dichromate paper appears to suffer from incomplete oxidation at higher NO_x concentrations and is also subject to difficulties in preparation.

Legend: ST = Static Tank   CR = Chevron Research
BM = Bureau of Mines   PDS = Phenol disulfonic acid

Fuel	Engine Operation	NO_x, ppm ST	BM	CR	PDS
Indolene	Cruise, 40 mph	297	311	—	—
	"	279	305	—	—
	"	331	349	—	—
	"	315	329	—	—
	California cycle	228	244	—	—
	"	246	276	—	—
	"	99	111	—	—
	"	250	278	—	—
	"	121	127	—	—
	"	270	283	—	274
	"	632	645	—	647
	"	632	647	—	657
	"	678	702	—	699
	"	229	237	225	220
	"	230	247	—	239
	Modified California cycle[a]	526	545	—	—
	"	513	521	500	496
	"	487	500	496	491
Isooctane	California cycle	113	119	—	109
	"	179	185	165	172
	"	113	118	—	113
	Modified California cycle[a]	417	—	—	427
	"	512	—	—	527
	"	653	—	—	633
	"	414	417	—	440
	"	360	369	375	348
Heavy with aromatics	California cycle	154	159	—	152
	"	235	244	225	227
	"	217	224	202	208
	Modified California cycle[a]	462	479	466	465
Heavy with olefins	California cycle	148	156	—	147
	"	195	198	186	185
	"	190	205	186	181
	Modified California cycle[a]	422	433	410	409

Table 4-2

Comparison of NO_x Results Obtained by Simultaneous Application of the ST, BM, CR and PDS Methods (7)

Some of the automotive exhaust sampling methods offer advantages over the conventional grab sampling methods. Collection in a 50 liter plastic bag allows integration over a 25 or 30 minute cycle and thereby increases the accuracy of the emission determination and decreases sampling errors due to source variation. An interesting feature of these automotive exhaust results is that the overnight absorption time of the conventional PDS method may be reduced by increasing the oxygen content of the collected sample.

4.3.5 Modified Saltzmann Method

4.3.5.1 Description

This method involves oxidation of NO to NO_2 in the gas phase by the excess oxygen in the sample. The NO_2 formed is absorbed in the Saltzmann reagent. (The chemistry of the Saltzmann method is discussed in detail in Section 4.5.1.) Davis and O'Neil (9) collect exhaust gas directly in an evacuated flask containing Saltzmann reagent as the absorbing solution. The diesel exhaust contains sufficient oxygen (10% or more) to oxidize all the NO to NO_2 within an hour. The PHS method involves grab sampling with a 100 cc syringe. The syringe is charged with 80 cc of Saltzmann reagent and 20 cc of gas is collected. The syringe is used as the reaction vessel. After 24 hours, the absorbance is measured at 550 nm and the NO_x concentration is computed.

4.3.5.2 Areas of Application

(a) Diesel exhausts (9), power plants (590).

(b) Nitric acid plants (173).

4.3.5.3 Sampling Equipment

(a) 250 cc evacuated flask containing 25 cc of Saltzmann reagent.

(b) 250 ml gas sampling tube or syringe.

4.3.5.4 Applicable Concentration Range

Wide if grab sampling techniques are used to increase the range.

4.3.5.5 Precision and Accuracy

Analysis of a series of 20 diesel exhaust samples with the modified Saltzmann method gives a coefficient of variation of 3.5% at 846 ppm NO_x for duplicate samples compared to 1.6% (838 ppm NO_x) for the phenol disulfonic acid method. Accuracy when compared to mass spectrometry is the same as PDS, ±5%.

4.3.5.6 Interferences

A major problem in this method is the interference from SO_2. A series of tests with synthetic mixtures of NO and SO_2 in air was conducted at NAPCA with the PDS and the Saltzmann methods (548). The NO and SO_2 concentrations are typical of those found in power plants. The PDS method shows no decrease in NO_x concentration as the SO_2 concentration is increased. The apparent NO_x concentration in the Saltzmann method, however, decreases markedly with concentration (Figure 4-4). This may be due to the reaction:

$$NO_2 + H_2SO_3 \rightarrow H_2SO_4 + NO$$

which occurs at the gas liquid interface (451). H_2SO_3 will be oxidized by the peroxide in the PDS method. Thus, SO_2 would have to be removed quantitatively for the Saltzmann method to product accurate results in coal- and oil-fired power plants.

4.3.5.7 Comments and Conclusions

This method may be useful for a rapid determination of NO_x in gas-fired power plants where SO_2 is not present. One should be able to obtain a rapid estimation by this method provided sufficient oxygen is present and the NO_x concentration is high. The stoichiometry remains a major problem.

4.3.6 Neutralization Methods

4.3.6.1 Description

The PHS hydrogen peroxide method (173) as well as the modified Galliard (DuPont) method (173) involve collection of gas samples in evacuated flasks containing dilute aqueous peroxide solution as the absorbent. The nitrogen oxides are oxidized to nitric acid, then determined by titration with standard sodium hydroxide solution using methyl red (PHS) or methyl purple (DuPont) indicators. In the DuPont method, a trace of cupric sulfate is added to increase the rate of absorption of nitric oxide.

4.3.6.2 Areas of Application

Nitric acid plants.

4.3.6.3 Sampling Equipment

(a) Evacuated flasks containing acidic peroxide as the absorbent (PHS).

(b) 300-500 ml gas sampling bulb; sample collected by displacement (DuPont).

4.3.6.4 Applicable Concentration Range

Has been used for high NO_x concentrations (> 500 ppm) only.

4.3.6.5 Precision and Accuracy

Given as ±0.12% at 20% NO based on 30 determinations in a weekly period by the same analyst. DuPont (173).

4.3.6.6 Interferences

Since it is a non-specific method (determines total acidity), any acidic (CO_2, SO_2), or basic compound in the flue gas will interfere.

4.3.6.7 Comments

In the PHS method, the sample flask is thoroughly shaken every ten minutes for the first half hour. After another half hour,[*] the sample is titrated with 0.01N NaOH. The DuPont procedure required the addition of peroxide and freshly prepared cupric sulfate solution to the gas sampling flask. The contact time is one hour.

Another non-specific method[†] is that developed by Johnson (450) for determining the oxides of nitrogen. This method involves reacting the oxides of nitrogen with a "mixed acid" of H_2SO_4 and HNO_3 to form $HNOSO_4$. After the sample is completely reacted, excess standardized $KMnO_4$ is added to oxidize the nitrous acid (HNO_2) to nitric acid according to the following reactions:

$$HNOSO_4 + H_2O \rightleftharpoons H_2SO_4 + HNO_2$$

$$2KMnO_4 + 5HNO_2 + 3H_2SO_4 \rightleftharpoons 5HNO_3 + 2MnSO_4 + K_2SO_4 + 3H_2O$$

This method has been used for high NO_x concentrations and is a non-specific method. Interferences such as SO_2 would be a major problem in fossil fuel-fired power plants (oil and coal).

4.3.6.8 Conclusions

The hydrogen peroxide method (PHS) may prove useful for a fast analytical readout in a gas-fired power plant where SO_2 is not present and the NO_x concentration is high.

4.3.7 Reactive Solid Sorbents

Solid sorbents for collection of oxides of nitrogen offer several advantages over conventional grab sampling techniques now in use:

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[*] Note the short oxidation time in this procedure is due to the very high NO (several thousand ppm) concentrations found in nitric acid plants.

[†] Not a neutralization method.

(1) Integration over long sampling times (30 to 60 minutes) provides more reliable and accurate measurement of the source strength. The resulting large sample permits replicate analyses to be performed for improved precision.

(2) The number of individual samples required may be reduced compared to grab sampling techniques; L.A. APCD requires taking NO_x samples in quadruplicate for PDS analyses.

(3) There is the possibility that a multi-pollutant collector for both NO_x and SO_x may be developed.

Peters and Straschil (570) have tested reactive solid sorbents for the simultaneous determination of NO and NO_2 or NO_x in mixed nitric acid plant off gases.* (Only determination of NO_x is discussed here; determination of NO and NO_2 is treated in Section 5.) The sorbents developed were $AgMnO_4$ and $NaClO_2$ supported on aluminum hydrate. These supported oxidants have a high surface area and are reported to react rapidly and quantitatively with both NO and NO_2. The resulting nitrate is determined by Devardas method (reduction to NH_3).

A brief discussion of potential solid sorbents for collection of SO_2 was given previously (Volume I). Much thermodynamic data and some kinetic results are available for the sulfur oxides from studies on the application of solid sorbents for SO_2 control processes. However, little data are available for the oxides of nitrogen. The reactive sorbents which appear promising for total NO_x determination are the metal oxide oxidants which were the most promising materials for SO_2 collection: PbO_2, MnO_2 and CeO_2.

The reactions of PbO_2 with oxides of nitrogen have been studied recently (391). Many previous workers have considered the reaction of nitrogen oxides with PbO_2 to be represented by the following equations:

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*This method has not been used in combustion flue gases which contain other active reducing agents.

$$2NO + PbO_2 = Pb(NO_2) \cdot PbO + 0.5\ O_2$$

and

$$2NO_2 + 2PbO_2 = Pb(NO_3) \cdot PbO + 0.5\ O_2$$

Mishmash and McLoan (391) reinvestigated these reactions by gas chromatographic and polarographic techniques. They found that chemical reaction rather than physical absorption does indeed occur. Evolution of oxygen was not observed; the product was divalent lead, as determined by polarography and spot tests. Mishmash and McLoan (391) rewrite the reactions as follows:

Nitrous oxide (N_2O)

$$PbO_2 + N_2O = \text{N.R.}$$

Nitric oxide (NO)

$$PbO_2 + NO = PbO + NO_2$$

$$2NO_2 + PbO_2 = Pb(NO_3)_2$$

Nitrogen dioxide (NO_2)

$$PbO_2 + 2NO_2 = Pb(NO_3)_2$$

Since they showed that oxides of nitrogen are quantitatively collected by a PbO_2 column, determination requires selection of a suitable method for analysis of NO_3^- in the PbO_2 matrix. One possibility is thermal decomposition (if it can be shown to be quantitative) as follows:

$$2Pb(NO_3)_2 \rightarrow 2PbO + 4NO_2 + O_2$$

The $NO_2 + O_2$ product resulting may be readily determined by a variety of techniques. Direct analysis by dissolution or leaching of the PbO_2 matrix is, of course, also feasible.

A possible advantage (and complication) of this technique is that SO_2 also reacts with the lead dioxide and would be retained as lead sulfate. This is the principle of the sulfation candle used frequently in ambient air SO_2 measurements. Thus, from one test, one might expect to obtain total NO_x and SO_x which are the major gaseous pollutants from fossil fuel combustion. Although these solid sorbents clearly require much developmental work, there are many possible advantages including ease of use and potential high precision multiple pollutant (NO_x and SO_x) determinations.

4.4 Analytical Methods Used for Determining Nitrate in Aqueous Solutions

4.4.1 Nitrate Electrode (317,390,417,435,439,440,441,607,612)

4.4.1.1 Description of Method

The nitrate-selective specification electrode (a liquid ion-exchange membrane electrode) and a reference electrode (calomel) are inserted into the aqueous nitrate sample. The potential difference between the electrodes is directly related to the nitrate concentration in the sample via a calibration curve prepared using aqueous nitrate standards.

4.4.1.2 Areas of Application

Nitrate in water (390,607) in plant materials (417,441), soil extracts (435,440), and microbiological media (439).

4.4.1.3 Applicable Concentration Range

From approximately 2 to 2200 ppm NO_2 assuming a 1-liter flue gas sample and 10 ml of absorbent solution. Higher concentrations can be obtained by dilution with more absorbent.

4.4.1.4 Accuracy and Precision

Coefficient of variation (C.V.) approximately 3% when using standards which bracket the unknown (317,417): C.V. = 2-3%

(435) and 3-6% (440) from analyses of a large number of soil extracts, and 1% when adding electrolyte to get high ionic strength (441). Use of a solid-state fluoride electrode and standard addition reported to have C.V. = 0.5-0.7 for measurement of nitrate solutions (612).

Electrode results agreed with the phenol disulfonic acid method within 10 to 15% in analysis of plant extracts (417), water (607), and with 2,4-xylenol method in analysis of soil extracts (435).

4.4.1.5 Interferences

Iodide, bromide, and some organic acids interfere (390,417) but these can be removed by ion-exchange (417). Since the electrode measures activity rather than concentration, changes in the ionic strength of the sample solution will result in variations in apparent concentration. This effect can be minimized by maintaining the ionic strength of the solution at a constant level with 1% sodium sulfate. This results in a slight loss in sensitivity (441).

The response to nitrite is only about 0.06 that of nitrate (390).

4.4.1.6 Comments

(a) The procedure is very rapid. Measurement of nitrate generally takes 1 to 2 minutes after equilibrium of the nitrate solution with the electrode.

(b) Interferences such as bromide and iodide can be removed via ion-exchange (417), if necessary.

(c) With a battery-operated, expanded scale pH meter, field analysis of nitrate would be simple provided that the absorption and oxidation time of NO can be reduced comparably.

(d) Effects of flue gas constituents such as SO_2 have not been checked.

(e) Electrode response was not changed and sensitivity decreased slightly when measurements were made in 0.07M sodium sulfate solution (441); this would indicate that the absorber solution now used with the PDS method could not be applicable.

(f) In the range of 2 to 9, pH appears to have little effect on the response (317).

4.4.1.7 Conclusion

This method should be investigated as an alternative to the nitration of organic reagents methods now in use (see Section 4.6).

4.4.2 1-Aminopyrene (7)

4.4.2.1 Description of Method

One volume of aqueous nitrate sample is added to three volumes of 0.01% 1-aminopyrene in concentrated H_2SO_4. The mixture is heated at 100°C for 15 minutes, cooled, and the absorbance is measured with a spectrophotometer at 456 nm. The color is stable for at least one hour.

4.4.2.2 Areas of Application

Aqueous extracts of airborne particulate matter.

4.4.2.3 Applicable Concentration Range

Up to 2.3 μg NO_2 (1.2 ppm NO_2 in 1 liter) so that aliquoting is necessary, the absorbance concentration curve is non-linear below ca. 1 μg NO_2.

4.4.2.4 Precision and Accuracy

Coefficient of variation = 4% and 6% for replicate measurement of 6.2 and 3.1 μg nitrate, respectively. No accuracy data.

4.4.2.5 Interferences

Nitrite gives nearly the same response as nitrate; iron (III) gives positive interference, but less than 1/20th that of nitrate.

4.4.2.6 Comments

(a) The reagent is more sensitive but less precise than most other colorimetric methods.

(b) It is likely to be oxidant-sensitive as shown by iron (III) reaction.

(c) Chemistry of reaction is unclear; lack of adherence to Beer's law may mean mixed product.

(d) This procedure is reasonably rapid compared to PDS and xylenols.

4.4.2.7 Conclusion

Since this high sensitivity is not needed for total NO_x measurements in flue gases, the relatively poor precision and other problems make this method unattractive as an analysis method for our purposes.

4.4.3 Chromatropic Acid (276,327)

4.4.3.1 Description of Method

Three ml of aqueous nitrate is mixed with 7 ml of 0.01% chromatropic acid (in concentrated H_2SO_4) and the resulting color is measured spectrophotometrically at 415 nm. Addition of 1% HCl to the H_2SO_4 in the reagent gave a higher absorptivity. An intense peak was reported at 357 nm (327) but this was not present in other investigations (276). The color is stable at least four days.

4.4.3.2 Areas of Application

None tested.

4.4.3.3 Applicable Concentration Range

Five to 55 ppm per liter gas measured at 415 nm in the absence of chloride; the 357 nm peak gives non-linear absorbance versus concentration curves in the 0 to 5 ppm NO_2 range.

4.4.3.4 Precision and Accuracy

No data.

4.4.3.5 Interferences

Nitrite gives a positive interference. Other interferences include: iron (III), bromide, chloride (if the chloride-containing reagent is not used), formaldehyde, bromate, chlorate, and iodate.

4.4.3.6 Comments

(a) The usefulness of the 357 nm peak is greatly impaired by the non-linear calibration curves. This peak may, in fact, be an artifact (276).

(b) The reagent appears to be oxidant-sensitive since iron (III) and halates interfere.

(c) Chloride-containing reagent would eliminate chloride interference found in most nitration reagents.

4.4.3.7 Conclusions

Chromatropic acid reagent might be useful if formaldehyde and oxidants do not interfere. Initial laboratory work, however, indicated that oxidants did interfere with this method. Another problem was the very broad absorption spectrum of the compound. Thus, this method was not investigated further (see Appendix 4).

4.4.4 Strychnidine (331)

4.4.4.1 Description of Method

An aqueous sample is mixed with an equal volume of strychnidine reagent (0.03% in concentrated H_2SO_4). The red color produced is allowed to develop for 20 minutes (±1 minute) and measured at ca. 540 nm with a spectrophotometer. The color is not stable.

4.4.4.2 Areas of Application

Trace nitrate in water.

4.4.4.3 Applicable Concentration Range

1.6 to 16 μg nitrate in a 5 ml sample.

4.4.4.4 Precision and Accuracy

No data.

4.4.4.5 Interferences

Nitrite.

4.4.4.6 Comments

The absorbance-concentration curve does not obey Beer's law, and the increase of absorbance with time necessitates a timed reaction.

4.4.4.7 Conclusion

The method is too tedious and problematic. It is not useful as other organic reagents.

4.4.5 Reduction of Nitrate to Nitrite with Cadmium (332)

4.4.5.1 Description of Method

An aqueous sample is buffered at pH 8 and passed through a column of amalgamated cadmium to reduce nitrate to nitrite. The nitrite is then determined by addition of sulfanilamide and 1-naphthyl-ehtylenediamine and spectrophotometric measurement at 540 nm.

4.4.5.2 Areas of Application

Trace nitrate in sea water.

4.4.5.3 Applicable Concentration Range

0.06 to 0.6 mg nitrate per liter (equivalent to from 8 to 85 ppm NO_2 per liter using 25 ml absorbent).

4.4.5.4 Precision and Accuracy

Coefficient of variation = 2% for replicate analyses of distilled water containing up to 0.6 mg nitrate per liter. No data are given on the accuracy.

4.4.5.5 Interferences

Nitrite.

4.4.5.6 Comments

(a) The reduction is a slow procedure (10 to 15 minutes through column), and the cadmium amalgum is tedious to prepare.

(b) This multi-step procedure is prone to errors.

4.4.5.7 Conclusions

Not enough advantages over organic nitration reagents to warrant consideration.

4.4.6 Diphenylamine-diaminodiphenylmethane (267)

4.4.6.1 Description of Method

An aqueous nitrate sample is mixed with 0.05% diphenylamine plus 2% diaminodiphenylsulfone in 60% H_2SO_4-10% H_3PO_4 and ca. 5 mg sodium chloride to give a blue color which is measured spectrophotometrically at 600 nm.

4.4.6.2 Areas of Application

Trace nitrates in H_2SO_4.

4.4.6.3 Applicable Concentration Range

0.25 to 3 μg nitrate per ml sample.

4.4.6.4 Precision and Accuracy

Coefficient of variation estimated to be 2 to 4%. No accuracy data.

4.4.6.5 Interferences

Peroxide is a positive interference but other oxidants are not.

4.4.6.6 Comments

(a) The complex is very sensitive to temperature (extinction coefficient varies about 3% per degree C).

(b) Nitrite does not react with this reagent.

4.4.6.7 Conclusions

This method has no advantages over other organic reagents; the temperature effect is very detrimental.

4.4.7 Diaminodiphenylsulfone (267)

4.4.7.1 Description of Method

An aqueous nitrate sample (1 ml) is added to 0.2% 4,4-diaminodiphenylsulfone in concentrated H_2SO_4 (3 ml) and heated at 100°C for two minutes. The solution is diluted to 25 ml with H_2O and the color is measured spectrophotometrically at 410 nm.

4.4.7.2 Area of Application

Aqueous nitrate samples.

4.4.7.3 Application Concentration Range

Twenty to 200 μg NO_2 per ml of absorbent (equivalent to 100 to 1,000 ppm NO_2 per liter using 10 ml of absorbent).

4.4.7.4 Precision and Accuracy

Coefficient of variation = 1 to 1.5% based on replicate analysis of aqueous samples containing from 30 to 300 μg nitrate. No accuracy data.

4.4.7.5 Interferences

Nitrite, bromide, halates give positive interferences: chloride negative interference; lower alcohols and esters cause negative interference.

4.4.7.6 Comments

(a) Reagent sensitive to oxidants and halides.

(b) Relatively less sensitive to nitrate than other reagents.

4.4.7.7 Conclusions

Reagent offers no special advantages over other organic reagents, and is apparently more subject to interferences.

4.4.8 Brucine (329)

4.4.8.1 Description of Method

An aqueous nitrate sample is mixed with aqueous brucine and concentrated H_2SO_4 to give a final mixture containing 0.04% brucine in 50% H_2SO_4. The mixture is stored in the dark, cooled to 30°C, and measured spectrophotometrically at 410 nm.

4.4.8.2 Areas of Application

Nitrates in soil extracts and water.

4.4.8.3 Applicable Concentration Range

Up to 50γ NO_2 (25 ppm NO_2 per liter sample).

4.4.8.4 Precision and Accuracy

No data.

4.4.8.5 Interferences

Nitrite is a positive interference but chlorides do not interfere.

4.4.8.6 Comments

The color is sensitive to reaction temperature, concentration of the acid, and exposure to light.

4.4.8.7 Conclusions

Method has no advantages over other organic reagents, and is considerably more tedious.

4.5 Analytical Methods Used for Measuring Nitrite Ion in Aqueous Solutions

4.5.1 Griess-Saltzmann Diazotization Coupling Reactions

4.5.1.1 Description

This method as generally used involves absorption of the NO_2 or N_2O_3 directly in the coupling reagent. Saltzmann's reagent has been the most widely used method for atmospheric monitoring (1,9,77,85,97,100,105,133,144,151,187,191,375,387,420,436). The Saltzmann reagent consists of 0.5% sulfanilic acid and 0.002N-(1-naphthyl) ethyenediamine in aqueous 14% acetic acid (133). Other coupling agents used include 1-naphthylamine (modified Griess Ilsovay) (176), phenol (used with sulfanilamide) (241), and N-(1-naphthyl) ethlenediamine dihydrochloride in aqueous H_3PO_4 (142,251) coupled with sulfanilamide.

After a short time (ranging from 15 to 60 minutes), the absorbance of the dye (formed by the diazotization reaction initiated by HNO_2) is measured at 540-560 nm with a spectrophotometer.

4.5.1.2 Areas of Application

Used mainly for atmospheric monitoring but modified methods have been used for diesel exhausts (9) (Section 4.3.5), oxides of nitrogen in flue gas (241), and nitric acid plants (Section 4.3.5).

4.5.1.3 Sampling

(a) Bubblers containing coupling reagent

(b) Bubblers containing 0.1N NaOH (241,172).

(c) $KMnO_4$ bubblers plus (3) bubblers containing Saltzmann reagent in series (436).

(d) (Grab sampling technique described earlier in Section 4.3.5.)

4.5.1.4 Applicable Concentration Range

Primarily for low NO_2 levels (with bubblers), however, the concentration range has been extended with grab sampling techniques for the higher NO_x concentrations (9,77).

4.5.1.5 Precision and Accuracy

Collection in three bubblers in series - coefficient of variation (C.V.) is 1.3-2.6% for gases containing 15 and 31 ppm NO_2 (436). Collection in 50 ml syringe - C.V. = 2-3% for 1260 ppm NO_2 in air (77).

Accuracy is very much in doubt because of the uncertain stoichiometry of hydrolysis and reactions of NO_2 and NO with the coupling reagent. Amounts of NO_2 required to give absorbance equal to known concentrations of $NaNO_2$ vary from 0.60 to 1.0 for up to 2 ppm NO_2 in air (77,109,133,151,191) using bubbler samples, and from 0.77 to 0.57 for 500 to 1400 ppm NO_2 (77,97) using grab samples. A recent grab sample study (611) has also shown the change in factor from 0.85 to 0.65 when NO_2 concentration increased from 500 to 2800 ppm.

Various investigators have compared the color intensity from mixtures of NO_2 and air (or N_2) with the color intensity from known amounts of $NaNO_2$ (in solution). Representative results illustrating the lack of agreement found using Saltzmann's reagent are summarized in Table 4-3.

4.5.1.6 Interferences

SO_2 results in loss of color, for example: 15 ppm SO_2 causes an 8% loss in 100 ppm NO_2 (436); 90 ppm SO_2 caused 4% loss in 2-3 ppm NO_2 (133), but the error could be minimized by measuring the solution within 45 minutes; 900 ppm SO_2 caused 11% loss in 2-3 ppm NO_2 (133). Addition of 1% acetone cuts loss due to SO_2 by a factor of 4 (133).

TABLE 4-3

REPORTED STOICHIOMETRICS FOR SALTZMANN REAGENT

Sampling Method	NO_2 Conc., ppm	NO_2 Source/Carrier Gas	Ratio: $\frac{\text{Mole } NaNO_2}{\text{Mole } NO_2}$	Reference No.
Bubbler	< 1	NO_2 cylinder/air	0.72	133
Bubbler (change in reagent)	< 1	NO_2 cylinder/air	0.72	85
Bubbler	1-2	N_2O_4/air	0.95	191
Bubbler	~ 1	NO_2 in air via dilution in bottles	0.60	109
Flask (syringe)	5	NO_2 from $PbNO_3$ in carboy	0.69	77
	1200	NO_2 from $PbNO_3$ in carboy	0.57	71
Bubbler	< 1	NO_2 in air stream	~ 1.0	151
Flask	500	NO_2/air in carboy	0.85	611
	2800	NO_2/air in carboy	0.65	611

NO does not react with the coupling reagent but it will if oxidized by O_2. Light exposure causes 20-25% loss in color after 24 hours (436). Storage in dark at 0°C reduces losses.

4.5.1.7 Comments

SO_2 interferences in flue gases is a major problem (Figure 4-4) with this method.

Many changes in the Saltzmann method have been made, i.e., use of isopropanol (100) instead of acetic acid, etc. (without enough extensive testing).

The stoichiometry problem has not been resolved to date.

4.5.1.8 Conclusions

This method has not been checked sufficiently for effect of real flue gas components. However, the SO_2 interference at levels found in flue gases has been shown to be a major problem of this technique. The SO_2 interference may be controlled by absorbing the gases directly in caustic rather than Saltzmann's reagent (see Section 3.3). Extent of oxidation of NO during sampling and reaction not known. Calibration (stoichiometry) factor for use of aqueous nitrite standard is uncertain; individual operators should check their results against known gas mixtures.

Overall, the method should not be used for flue gases which contain sulfur dioxide.

4.5.2 Other Diazotization-Coupling Reagents for Nitrite

4.5.2.1 Description

These reagents are generally composed of a diazotizable amine and a coupling agent (also generally an amine) which may be added simultaneously or sequentially to the aqueous nitrite sample. The resulting colored azo compounds are measured spectrophotometrically.

Sawacki, et al. have published two comprehensive reviews and listings of diazotization reagents for nitrite (326, 362). Table 4-4 lists the reagents noted by them (326) and gives the colors which are stable for at least one hour and capable of detecting 6 micrograms of nitrite (equivalent to 1 liter of gas containing 3 ppm (v/v) of NO_2). Saltzmann's reagent is included for comparison.

Shinn used sulfanilamide and N-(1-naphthyl)-ethylenediamine for the colorimetric measurement of trace aqueous nitrite in the range of 0.05 to 1 microgram per ml sample (177).

Another reagent proposed for nitrite is a mixture of p-diamino-diphenylsulfone and diphenylamine in ethanol containing nitric acid which gives a yellow color (277). The Beer's law range is 0.3 to 8 micrograms nitrite per ml of sample.

The use of (4-aminophenyl)-trimethylammonium salts as the diazotizable amine and N,N-dimethyl-1-naphthylamine as the coupling agent has been proposed as a reagent for aqueous nitrite with a Beer's law range of 3 to 45 micrograms per ml in a sample (255).

4.5.2.2 Application

Most of these reagents have not been tested to any great extent. The p-nitroaniline/azulene reagent has been applied to measurement to trace nitrite in water (268). This reagent also gave a similar color when NO_2 was bubbled through it, but no quantitative measurements were made.

4.5.2.3 Applicable Concentration Ranges

As noted under 4.5.2.1, the reagents are theoretically capable of measuring 3 ppm NO_2 per liter sample.

4.5.2.4 Precision and Accuracy

No data on flue gas analysis.

TABLE 4-4

DIAZOTIZATION-COUPLING REAGENTS FOR NITRITE

Amine	Coupler	Maximum (nm)	Beer's Law Range (µg NO_2 in sample taken)
p-phenylazoaniline	1-naphthylamine	643	0.7-20
4-nitro-1-naphthylamine	1-anilinonaphthalene	695	0.6-15
p-phenylazoaniline	benzaldehyde + 2-benzothiazolyhydrazone	590	0.8-20
p-phenylazoaniline	none added	595	0.8-16
p-nitroaniline	azulene	515	0.4-9
anthranilic acid	1-anilinonaphthalene	571	0.4-9
p-nitroaniline	benzaldehyde + 2-benzothiazolylhydrazone	595	∿ 1-20
sulfanilic acid (Saltzmann's reagent)	N-(1-naphthyl)-ethylene-diamine	550	2.5-60

4.5.2.5 Interferences

Oxidants such as chlorine are general interferences.

4.5.2.6 Comments

Any one of these reagents might be used for measurement of nitrite, once it is trapped, but none would appear to hold any advantage over the Saltzmann reagent with regard to stoichiometry.

4.5.2.7 Conclusions

No reason to prefer any of these over the Saltzmann reagent.

4.5.3 Spectrophotometric Determination of Nitrite in Aqueous Solutions (69,621)

4.5.3.1 Description

The nitrite ion has been measured directly in aqueous solutions by spectrophotometry at 355 nm (69) after absorption of NO_2 in 10% potassium hydroxide solution. The simultaneous measurement of both nitrate and nitrite in aqueous solution at varying pH's has been reported (621).

4.5.3.2 Areas of Application

High concentrations of NO_2 in N_2 (69).

4.5.3.3 Applicable Concentration Range

Used for measurement of a few hundred up to several thousand ppm NO_2 (69).

4.5.3.4 Precision and Accuracy

No useful data.

4.5.3.5 Interferences

This is actually a non-specific method since any substance which absorbs in the near UV spectral region is a potential interference (aromatic compounds, ketones, etc.).

4.5.3.6 Comments

Collection in strongly alkaline solution apparently gives a constant stoichiometry ratio of 0.5 mole nitrite per mole NO_2 (69), which would be an improvement over the direct collection situation where the stoichiometry is uncertain (see Section 3.3).

The SO_2, CO_2, and other acidic species in the flue gases will be rapidly absorbed by the alkaline solution. These may result in changes in alkalinity, and, hence, in stoichiometry.

4.5.3.7 Conclusions

Probable interferences in flue gases as well as the limited sensitivity make this method unattractive for present purposes.

4.6 Nitrate Electrode Studies

4.6.1 Introduction

In view of the tedious nature of the phenol disulfonic acid (PDS) technique for NO_x (discussed earlier), several alternate approaches were considered for the determination of nitrate ion in aqueous solutions. The chromatropic acid method seemed to be an obvious improvement, however, preliminary laboratory work (Appendix 4) was not encouraging. Therefore, considerable effort was spent on a feasibility study of the nitrate electrode. This included ease of maintenance, durability, reliability, accuracy, sensitivity, and the relative interference produced by other species. Since sulfate proved to be a problem in a previous study (548), we evaluated a variety of methods for the removal of sulfate ion from the solution. The results are discussed in the following sections.

4.6.2 Electrode Assembly

Work has been conducted with an Orion Research nitrate electrode (Model No. 92-07). No substantial problems were encountered in assembling and filling the electrode. However, it is necessary to center the membrane disk in order to get an effective seal on the exchanger reservoir.

4.6.3 Reference Electrodes

In the initial work we used a saturated calomel electrode (SCE) as the reference electrode. In very dilute nitrate solutions (10^{-4}M), a sleeve-type electrode repeatedly produced discernible drift toward more negative potentials (increasing nitrate activity). This drift was probably due to leakage of the concentrated KCl electrolyte, since chloride ion does give a response approximately 0.06 times that of nitrate. A fiber-tip SCE, however, was found to perform satisfactorily.

4.6.4 Electrode Response and Performance

The sensitivity of the nitrate electrode and the repeatability of the nitrate electrode-SCE pair were evaluated by measuring the potential developed in dilute (10^{-1} to 10^{-5}M) solutions of nitric acid in distilled water prepared fresh daily by diluting 1.0M stock solution. The measurements were made with either a Beckman Expandomatic pH meter or an Orion Model 701 digital millivolt meter.

Immediately after assembly, the electrode often had a sensitivity of 59 to 60 mV per tenfold change in nitrate concentration over the range of 10^{-1} to 10^{-4}M and slightly less (ca. 45-50 mV) in the 10^{-4} to 10^{-5}M range. After a few measurements had been made, the sensitivity decreased to 55 to 56 mV per tenfold concentration change and remained at this level for at least two weeks. This sensitivity of 55 to 56 mV is in the range previously reported for the electrode.

Table 4-5 shows the variation in response of the electrode vs concentration found in measurements of the nitric acid

TABLE 4-5

REPRODUCIBILITY OF NITRATE STANDARDS

		Readings (mV)			Calibration Slope[a]				"Error" in Measuring 10^{-3} Calibration Solution[c]		
		Nitrate Concentration									
Date	Run No.	10^{-2}M	10^{-3}M	10^{-4}M	A	B	C	Av.	mV From Av. Slope[c]	mV Measured	mV Deviation
4/9	A	38.5	92.5	144.5	53	51.5		52.3	91	92.5	+1.5
	B	37	90.5	140					89	90.5	+1.5
4/10	A	34.5	87	138.5	52	53.3	52.5	52.6	87	87	0
	B	23.5	76.5	129					76	76.5	+0.5
	C	22	74.5	127					74.5	74.5	0
4/13	A	17.5	67.5	115.5	49			(49)	66.5	67.5	+1
4/14	A	9.5	63.5	122.5	56.5	54.8		55.7	65.0	63.5	-1.5
	B	14	67	123.5							
4/16	A	46	102	157.5	55.8	55.5	55.3	55.5	101.5	102	+0.5
	B	46.5	101.5	157.5					102	101.5	-0.5
	C	46.5	101.5	157					102	101.5	-0.5
4/24	A	46.5	103	157	55.3	56	56	55.8	102.5	103	+0.5
	B	45.5	100	157.5					101.5	100	-1.5
	C	45	100	157					101	100	-1
4/30	A	43.5	98	155	55.8			(55.8)	99.5	98	-1.5
5/1	A	43.5	99.5	155.5	56	56.8		56.4	100	99.5	-0.5
	B	43	98	156.5					99.5	98	-1.5
	σ(mV)[b]	3.4	3.4	3.1							

Average "error" = -0.2 mV
Standard Deviation = ±1.0 mV

---

a. Calculated from:

$$\frac{mV_{10^{-4}M} - mV_{10^{-2}M}}{2}$$

TABLE 4-5 (continued)

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b. Calculated from:

$$S = \sqrt{\frac{\Sigma(X_i - \overline{X})^2}{\Sigma \text{ d.f.}}}$$

where: X_i = individual readings

$\overline{X}$ = average mV reading for that day

d.f. = number of degrees of freedom for that day (number of measurements -1)

c. Assumes that 10^{-2} M calibration point was accurate. Calculated by adding the average calibration slope (mV per 10-fold concentration change) to the 10^{-2} M readings and rounding to the nearest 0.5 mV.

calibration solutions over a two-week period. In performing this study, measurements were made on aqueous solutions containing 10^{-2}, 10^{-3}, and 10^{-4}M nitric acid concentrations. When the response became erratic, we renewed the electrode. It can be seen that the electrode performs very reproducibly.

With a slope of 56 mV change in potential per tenfold change in nitrate concentration, a difference of 1 mV corresponds to an error of 4.3% in concentration. Since, as shown in Table 4-5, the absolute potential can vary over a few mV, it will be necessary to check calibration standards frequently in order to minimize measurement uncertainty.

The standard deviation of the variation in potential readings for any one day is nearly the same (3.4-3.1 mV) for all three concentration ranges. This represents more than 10% error, clearly showing that frequent standardization during the day will be needed in order to achieve acceptable precision (i.e., within a few percent relative error). The benefit of frequent "bracketing" calibration is shown by a calculation of the "error" (uncertainty) in the measurement of the 10^{-3}M calibration solution. For this calculation, we have assumed that the 10^{-2}M solution was accurate, and calculated the mV reading expected for 10^{-3}M nitrate. The average error found (-0.2 mV) and the standard deviation (±1.0 mV) for the "error" in any one measurement, are much lower than those of the raw data. As noted previously, for a slope of 56 mV per tenfold concentration, a 1 mV error corresponds to a relative error of 4.3% in concentration.

In connection with methods for determination of NO_2 by caustic absorption (Section 5.3), the response of the nitrate electrode was determined at pH 11.5. The system was calibrated by preparation of standards containing known concentrations of KNO_3 dissolved in .005N NaOH. The response observed in NaOH is very close to that in pure water to concentrations down to 10^{-3}M nitrate ion. At lower concentrations of nitrate ion in the caustic solution, the response (millivolts/decade) decreases rapidly so that the effective lower limit for the analysis at pH $\approx$ 11.5 is $\sim 5 \times 10^{-4}$M nitrate ion (EMF vs .005N NaOH $\approx$ 20 mV). In neutral (pH $\approx$ 7.5) and acid (pH $\approx$ 4.5) solutions the EMF response remains linear vs log (NO_3^-) down to 10^{-5}M, dropping rapidly at lower concentrations so that the effective sensitivity limit (EMF vs nitrate-free solution $\approx$ 20 mV) is 10^{-5}M NO_3^-. In dilute basic solution, electrode response in the range 10^{-1} to 10^{-3}M NO_3^- is Nernstean (58 mV/decade).

It is necessary to stir the solutions in order to obtain steady potentials. If the solutions are not stirred, the potentials tend to drift in a negative direction by 10 to 20 mV.

4.6.5 Direct Measurements on Solutions Used for Collection of Nitrogen Oxides

The data of Table 4-6 show the response of the nitrate electrode to various concentrations of nitric acid in 0.1N sulfuric acid containing 0.03% hydrogen peroxide (the absorbing solution used in the phenol disulfonic acid (PDS) method for nitrogen oxides).

TABLE 4-6

ELECTRODE RESPONSE IN 0.1N SULFURIC ACID/0.03% HYDROGEN PEROXIDE

HNO_3 Concentration (M)	Electrode Response (mV vs SCE) 0.1N H_2SO_4/0.03% H_2O_2		H_2O	
	Reading	"Slope Factor"	Reading	"Slope Factor"
10^{-1}	- 28		- 18.5	
		63		57
10^{-2}	+ 35		+ 38.5	
		56		54
10^{-3}	+ 91		+ 92.5	
		32		52
10^{-4}	+123		+144.5	
		0		46.5
10^{-5}	+123		+191	

The response of the electrode to the same nitric acid concentrations in aqueous 0.03% hydrogen peroxide was identical to that for water alone, so that the sharp decrease in response below 10^{-3}M nitrate is apparently due to the sulfuric acid.

This decrease can probably be attributed either to response of the electrode to sulfate and bisulfate (the electrode response to sulfate is approximately 0.006 times that for nitrate). It is apparent from these data that direct measurement of the PDS scrubber solution is not very useful for low nitrogen concentrations, since the lower limit of 10^{-3} nitrate necessary for accurate measurement corresponds to approximately 220 ppm of nitrogen oxides for a 1-liter gas sample absorbed into 10 ml of solution.

4.6.6 Effect of Sulfate on Nitrate Electrode Response

In order to gain a clearer idea of the extent to which the presence of sulfate influences the response of the nitrate electrode, the potential of this electrode was studied in a series of aqueous mixtures of H_2SO_4 and HNO_3, designed to simulate the absorbing solution from a range of flue gas compositions. The results, shown in Table 4-7, indicate that in the range of mole ratios of 50:1 and 100:1 sulfate to nitrate, the sulfate begins to cause substantial positive error in the measured nitrate concentration. This interference is presumably due to a positive response of the electrode to sulfate rather than to an ionic-strength effect, since increasing ionic strength (more sulfate) should cause a decrease in apparent nitrate activity. The 50:1 sulfate:nitrate limit corresponds to a flue gas containing approximately 3500 ppm sulfur oxides and 70 ppm nitrogen oxides, so that sulfate interference may be a problem only in the extreme case of high sulfur fuel and very low values of nitrogen oxides.

This problem of a serious positive interference by sulfate at molar ratio of greater than 50:1 over nitrate has also been noted by Orion Research. In view of the interference from sulfate, we tried a number of approaches for the removal of sulfate. These are described in the following section.

TABLE 4-7

EFFECT OF SULFATE ON NITRATE ELECTRODE MEASUREMENT

Added		Found			S and N oxides added - expressed as ppm in 1 liter sample[a]	
H_2SO_4 (M)	HNO_3 (M)	HNO_3 (M)	% Difference in HNO_3	Mole Ratio $SO_4^=/NO_3^-$	SO_x	NO_x
2.5×10^{-4}	1.0×10^{-3}	1.0×10^{-3}	0	0.25	140	560
1.25×10^{-3}	1.0×10^{-3}	9.9×10^{-4}	- 1	1.25	700	560
2.5×10^{-4}	1.0×10^{-4}	1.15×10^{-4}	+ 15	2.5	140	56
2.5×10^{-4}	1.0×10^{-3}	9.7×10^{-4}	- 3	2.5	140	560
2.25×10^{-3}	1.0×10^{-4}	9.4×10^{-5}	- 6	22.5	1260	56
5.0×10^{-3}	1.0×10^{-4}	8.5×10^{-5}	- 15	50	2800	56
5.0×10^{-3}	5.0×10^{-5}	1.03×10^{-4}	+ 100	100	2800	28
1.0×10^{-2}	1.0×10^{-4}	1.6×10^{-4} 1.52×10^{-4}	+ 60 + 52	100	5600	56
1.0×10^{-2}	5.0×10^{-5}	1.4×10^{-4} 1.15×10^{-4}	+ 180 + 130	200	5600	28
2.0×10^{-2}	5.0×10^{-5}	1.7×10^{-4}	+ 240	400	11200	28
5.0×10^{-3} [b]	1.0×10^{-4}	1.03×10^{-4}	+ 3	50	2800	56
1.0×10^{-2} [b]	5.0×10^{-5}	7.7×10^{-5}	+ 55	200	5600	28

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a. ppm (μℓ/ℓ) based on a 1 liter sample absorbed into 25 ml of solution.
b. Sulfate added as K_2SO_4 instead of H_2SO_4.

4.6.7 Sulfate Removal

Sulfate may be removed by precipitation of an insoluble sulfate salt, for example, with barium. Since the electrode also responds to many anions, we decided to use a system where the end product was an anion which gave a minimum response, e.g., monohydrogen phosphate. An excess of solid $BaHPO_4$ (prepared from barium hydroxide and phosphoric acid) was added to aqueous solutions of nitric acid of various concentrations, and to two concentrations of sulfuric acid containing nitric acid, and then the potential of the nitrate electrode was measured for each solution. The data are shown in Table 4-8.

The data in Table 4-8 indicate that removal of sulfate by direct addition of barium phosphate, or any more soluble barium salt, does not allow accurate measurement of nitrate with the electrode. It was thought that barium carbonate might work as a substitute because the liberated CO_2 could be removed by boiling of a dilute acid (0.001M) solution. Aqueous solutions containing various concentrations of H_2SO_4 and HNO_3 were prepared to cover a range of concentrations of sulfate and nitrate, and the apparent nitrate content was measured with the electrode. These solutions were treated with powdered $BaCO_3$ (0.6 g per 25 ml of solution), boiled for four minutes, cooled, diluted back to volume, and measured again with the nitrate electrode. The results are given in Table 4-9.

The data in Table 4-9 indicate that addition of $BaCO_3$, and subsequent boiling, did not result in a simple and immediate removal of sulfate. The increase in the measured nitrate concentration in two tests may be an indication that the boiling period was too short to remove all the bicarbonate, although Kolthoff and Sandell reported that five minutes of boiling is sufficient to remove 5×10^{-3} moles of CO_2 from 50 ml of solution. In any case, this does not appear to be an attractive approach for removal of sulfate.

To test the possible use of anion exchange for selective removal of sulfate from the absorbent solutions, we used a strong base resin, to hold up sulfate and other multivalent ions and let nitrate pass

TABLE 4-8

EFFECT OF ADDITION OF $BaHPO_4$ ON ELECTRODE RESPONSE

Concentration of HNO_3 (M)	H_2O	H_2O + $BaHPO_4$	0.012 M H_2SO_4[a] + $BaHPO_4$	0.0036 M H_2SO_4[a] + $BaHPO_4$	Average Apparent Nitrate Concentration (M)	% Error
10^{-1}	-8.5	-6.5	∇	∇	--	--
10^{-2}	+46	+50.5	∇	∇	--	--
10^{-3}	+102.5	+103.5	111.5	+110	7×10^{-4}	-30%
5×10^{-4}	∇	∇	+128	+129.5	3.3×10^{-4}	-35%
10^{-4}	+157.5	+157.5	+173.5	+168	5.3×10^{-4}	-45%
5×10^{-5}	+171.5	+171.5	∇	∇	--	--

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a. H_2SO_4 concentrations correspond to those expected for absorption of 1 liter samples containing approximately 2700 and 2400 ppm of SO_2 absorbed into 10 ml and 30 ml (0.012 M and 0.0036 M, respectively) of absorbing solution.

b. Calculated from the average mV reading for the two H_2SO_4 solutions.

∇ = Not measured

TABLE 4-9

EFFECT OF $BaCO_3$ ON MEASUREMENTS WITH THE NITRATE ELECTRODE

Added			HNO_3 Found			
			Before $BaCO_3$		After $BaCO_3$	
H_2SO_4 (M)	HNO_3 (M)	Mole Ratio $SO_4^=/NO_3^-$	HNO_3 (M)	% Error	HNO_3 (M)	% Error
2.5×10^{-4}	1.0×10^{-3}	0.25	1.0×10^{-3}	0	9.9×10^{-4}	-1
1.25×10^{-3}	1.0×10^{-3}	1.25	9.9×10^{-4}	-1	9.7×10^{-4}	-3
2.5×10^{-4}	1.0×10^{-4}	2.5	1.15×10^{-4}	+15	1.3×10^{-4}	+30
2.5×10^{-3}	1.0×10^{-3}	2.5	9.7×10^{-4}	-3	9.3×10^{-4}	-6
5.0×10^{-3}	1.0×10^{-4}	50	8.5×10^{-5}	-15	1.7×10^{-4}	+70
1.0×10^{-4}	1.0×10^{-4}	100	1.5×10^{-4}	+50	5.0×10^{-5}	-50
1.0×10^{-2}	5.0×10^{-5}	200	1.15×10^{-4}	+130	8.8×10^{-5}	+76

through for measurement. A 9 cm x 0.8 cm^2 column of Amberlite IRA-410 (20/50 mesh) was washed with 1N HCl, H_2O, 1N NaOH and H_2O until the effluent was neutral and free from chloride.

To test the ion-exchange take-up of sulfate, we applied 10 ml of 0.025M K_2SO_4 (equivalent to 1 liter of gas containing 5000 ppm SO_2) and then washed with 20 ml of H_2O. After 4 ml of K_2SO_4 solution had passed through, the column effluent became strongly alkaline, indicating displacement of hydroxide from the resin, but no sulfate was detected in the effluent. At the end of the 20 ml H_2O wash, the column effluent had become neutral.

A solution (1 ml) of 0.01M KNO_3 (equivalent to 1 liter of gas containing 225 ppm NO) was applied to the column, and washed with 10 ml of H_2O. After 3 ml of wash had been applied, the column effluent became alkaline (pH greater than 10), indicating that hydroxide was being displaced by nitrate. Since the hydroxide form of the resin takes up nitrate as well as sulfate, this anion exchange approach does not appear to be feasible.

4.6.8 Alternate Approaches for Sulfate Removal

An alternate approach to the nitrate electrode was needed since the original PDS absorbing solution gave increased sensitivity at the high sulfate levels (0.1N) and methods for the removal of sulfate by precipitation with barium salts or ion exchange proved unsuccessful. The effect of sulfate on the nitrate electrode potentials (Table 4-7) showed clearly that fairly high levels of SO_2 (sulfate) could be tolerated without major interference with the nitrate electrode potential. Therefore, we investigated the use of the nitrate electrode with a new absorbing solution, e.g., neutral 0.1% hydrogen peroxide. Samples were taken in a gas-fired home heating unit using the neutral peroxide absorbing solution. In order to check this technique, PDS samples were taken at the same time. The results are shown in Table 4-10 below.

TABLE 4-10

COMPARISON OF NITRATE ELECTRODE RESULTS WITH PDS

ppm NO_x (nitrate electrode)*	ppm NO_x (PDS)	% Recovery $\frac{\text{electrode}}{\text{PDS}}$ x 100
25	37	67
27	44	62

*Neutral (pH 7.0) peroxide absorbing solution

These low results are presumably due to the incomplete oxidation of nitrite in neutral solution. Therefore, we acidified the solution with sulfuric acid and repeated the measurement. For a pH adjusted to the range 2 to 3, we obtained good agreement between the nitrate electrode and PDS measurements (Table 4-11)

TABLE 4-11

COMPARISON OF NITRATE ELECTRODE AND PDS RESULTS FOR NO_x

ppm NO_x (nitrate electrode)*	ppm NO_x (PDS)
41	37
42	44

*pH 2.5

In view of the good agreement between nitrate electrode and PDS, we ran a number of tests on the nitrate electrode. These are described in the following section.

4.6.9 Test Results for the Measurement of NO_x in Flue Gas Samples with a Nitrate Ion Selective Electrode

In order to determine the feasibility of the nitrate electrode for measuring nitrogen oxides (as nitrate following oxidation and absorption steps), we have compared this technique to the phenol disulfonic acid (PDS) method for several combustion sources. The samples were collected in 2-liter evacuated flasks. The absorbing solution for the nitrate electrode samples was 25 cc of 0.003N H_2SO_4-0.3% H_2O_2. The PDS absorbing solution was 25 cc of 0.1N H_2SO_4-0.06% H_2O_2. The flue gas samples were collected in the evacuated flasks and allowed to stand overnight. The nitrate electrode samples could be measured immediately after absorption was complete. The PDS samples had to be evaporated, reacted, etc., and required 5 to 6 hours before the analysis was complete. The results of these tests are given in Table 4-12. The agreement between the two methods is excellent, i.e., within ±4% of the mean of the two methods.* When one considers that this difference represents errors in sampling as well as analysis, these results are encouraging.

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*Note that neither method yields results which are consistently low.

TABLE 4-12

COMPARISON OF PDS AND NITRATE ELECTRODE RESULTS FOR NO_x IN COMBUSTION EFFLUENTS

Test No.	ppm NO_x (nitrate electrode)	ppm NO_x (PDS)	Source
1	42	37	Gas-fired home heating unit run at low excess air
2	41	44	
3	229	217	Tangentially-fired (oil) boiler at 500 MW power plant with 1310 ppm SO_2 in effluent
4	168	181	
5	137	155	
6	132	129	Oil-fired unit (home heating) with 150 ppm SO_2 in the effluent
7	116	104	
8	52	53	

5. SAMPLING AND ANALYSIS METHODS FOR THE DETERMINATION OF NO_2 AND/OR NO

5.1 Introduction

Although a number of NO_2 measurements in fossil fuel-fired effluents have been reported (512,590), it is not clear that the measurements made were, in fact, NO_2 measurements. In one case (512), the NO_2 determination was by the PDS method, apparently based upon rapid absorption. NO_2 (?) concentrations were reported as 6 to 8% of the NO concentrations (589). The contact time is quite important as indicated, e.g., Equation 12 (Section 3.3.1.1). The time is very crucial. Unless very short absorption times were used, < 2 min., the error due to oxidation of NO would be significant. Unfortunately, we cannot determine the procedures utilized.

Another method, used by Lee, et al. (590) determines NO_2 (?) by the modified Saltzmann method (9). The major problems in application of this method, however, are major interference by SO_2 (see Figure 4-4) and the uncertain stoichiometry. A further problem in these measurements is presented by the contact time. Presumably, the contact time is long since their results reveal that NO_2 (?) concentrations apparently increase with the initial oxygen concentration, suggesting the possibility of NO oxidation.

Similar critical evaluations could be made where NO/NO_2 measurements have been attempted by others. Insofar as we have been able to determine, no reliable NO_2 measurements have been made in power plants effluents.

5.2 Sampling

For collection of total NO_x samples, very simple probes have been used (Section 4.2) since NO is the major nitrogen oxide present and its solubility in water is very small. This procedure is not valid where NO_2 is sought, since it is both a minor component and is, in addition, fairly soluble in water. Therefore, for collection of a sample for NO or NO_2 determination, as opposed to a total NO_x sample, the probe should be heated to stack temperatures to prevent changes in the gas composition by loss of NO_2 due to absorption in the condensate.

5.3 Sample Collection and Analysis

Several options exist for collection and analysis of NO and NO_2. These include use of solid sorbents, aqueous absorbents or kinetic analysis. The alternatives are discussed in the following sections.

5.3.1 Solid Sorbents

Peters and Strachil (570) have developed and tested two classes of solid sorbents: supported oxidants (discussed in Section 4.3.7 for total NO_x determination) and supported alkali carbonates. Sodium carbonate supported on an aluminum hydrate substrate reacts rapidly and quantitatively with NO_2 and ($NO + NO_2 = N_2O_3$) but does not react with excess NO (570). The supported carbonate must be "poisoned" to prevent catalytic oxidation of "excess" NO by air.

The principle of the analysis is based upon the formation of equimolar amounts of NO_2^- and NO_3^- upon absorption of NO_2 in alkali, compared to the formation of pure NO_2^- upon absorption of N_2O_3. Peters and Strachil (570) determine NO_2^- by $KMnO_4$ titration and total NO_3^- (after $KMnO_4$ oxidation) by Devardas method.* A third determination, for excess non-absorbed NO, is also required to complete the analysis and is obtained from the secondary absorbent ($NaClO_2$ - see Section 4.3.7). The authors suggest (570) that a significant advantage to the use of solid sorbents in the primary absorption step is the rapid reaction rate which permits precise determination of the time of sampling for a reacting (i.e., oxidizing) mixture containing $NO + O_2$.

Another approach is the use of inert solid absorbents (such as silica gel) as the NO_2 collector. Silica get appears to be a good candidate for collection of NO_2 and separation of NO. Gill (77) using 4 g of silica get for collecting NO_2 in the presence of NO, reported efficiencies of 40% in the range 15 to 60 ppm NO_2. At NO concentrations as high as 200 ppm, no more than 2 ppm is absorbed. Gill's measurements were apparently made at room temperature. An obvious way to increase the absorption efficiency of silica gel for NO_2 is to reduce the absorbent temperature.

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*These analytical methods are not recommended for flue gas analysis, however; see previous discussion of analytical methods.

Due to the limited time and effort, it was decided that the aqueous absorbents would be more fruitful (e.g., require less development) for NO_2. Thie approach is discussed in the following section.

5.3.2 Aqueous Absorbents

5.3.2.1 Introduction

The primary and secondary absorption approach to NO_2 analysis may also be conducted by use of more conventional aqueous absorbents. Peters and Strachil (570) recommend 0.1N NaOH for the primary adsorption and report complete separation of NO_2 and NO provided that both gas and solution phases are well stirred and adequate reaction time is employed. A grab sample may be taken in an evacuated flask, e.g., Figure 4-1 (bottom), containing 0.1N NaOH as the absorbent. After the sample is shaken for 5 to 10 minutes, the liquid containing the absorption products arising from N_2O_3 is drawn off. The gas sample is retained for an analysis of "excess" NO. The nitrate component of the liquid sample may be determined from an aliquot by a nitrate method. The nitrite component may be determined in the caustic solution by the Saltzmann method since sulfite will not reduce nitrite in alkaline solutions or by permanganate titration as recommended by Peters and Strachil (570). The "excess" NO in the grab sampling flask could be determined spectrophotometrically as NO_2 after oxidation in the gas phase (since all the SO_2 will be absorbed in the caustic solution) or by addition of an aqueous peroxide absorbent and subsequent measurement of total nitrate by the PDS or nitrate electrode methods. Thus, the original NO and NO_2 concentrations may be determined from the results of the two-stage absorption.

5.3.2.2 Experimental

The apparatus used for the two-stage absorption studies is that of reference (96) without the limiting orifice. Twenty-five ml of 0.005N NaOH was pipetted into a clean (calibrated) 2-liter flask. The flask was evacuated and the initial pressure was recorded. Samples of NO were prepared using the dilution system shown in Figure 5-1a. The NO_2 was prepared initially using a lecture bottle of NO_2 as the source and the dilution system in Figure 5-1a. This system required a heated flowmeter to eliminate condensation of NO_2. The NO and NO_2 flowmeters were calibrated using a soap film flowmeter. The NO calibration remained constant over long periods of time, however, the NO_2 calibration changed and yielded irreproducible NO_2 concentrations. Therefore, we eliminated the tank NO_2 and used an NO_2 permeation tube (Figure 5-1b). The evacuated flask was filled from the sampling line over a two to three minute period and the final pressure was recorded after periodic shaking during the specified absorption time. The contents were poured out and the flask was rinsed with an additional 25 ml of .005N NaOH which was added to the initial solution.

Analysis for nitrate was performed using the nitrate electrode and phenol disulfonic acid (PDS) method (described in the following section).

The concentration of NO_2 in ppm was calculated in the volume originally sampled at the sampling temperature (24.5°C) corrected to standard pressure by the following equation:

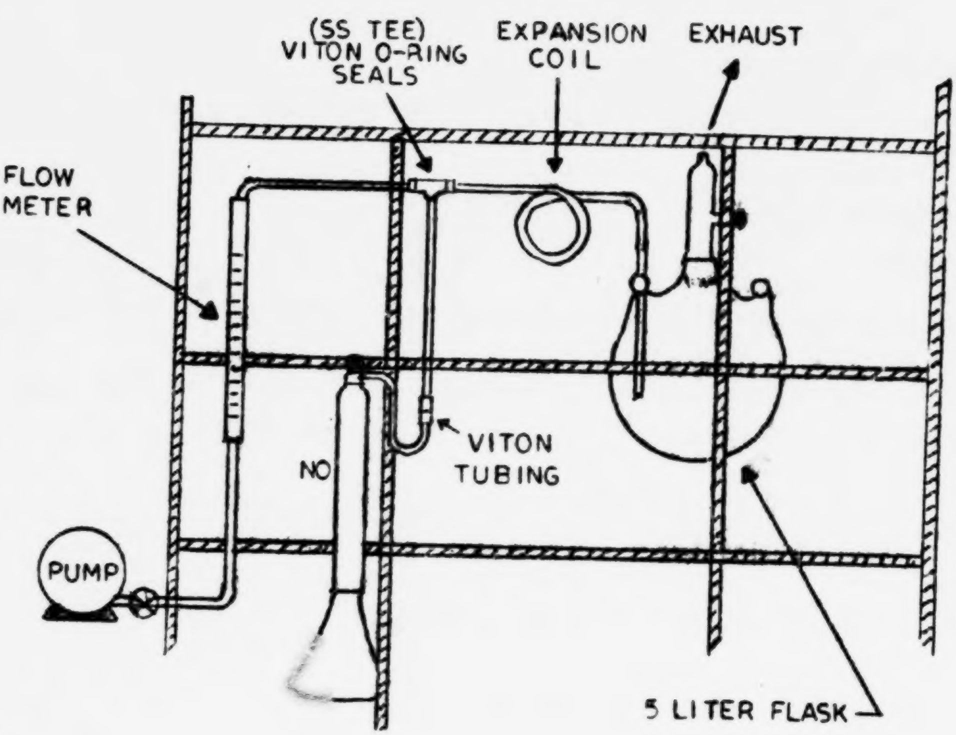
$$NO_2\ (\text{ppm}) = \frac{m\ v\ T\ P_o\ V_m\ f}{V_f\ T_o\ \Delta P}$$

where m = NO_3^- ion concentration, moles/l

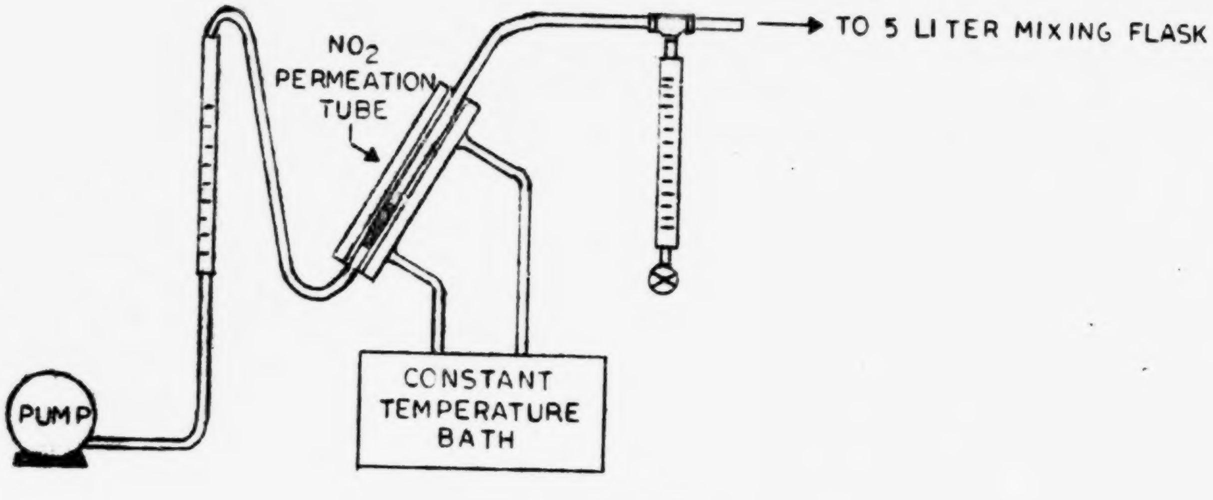
V = NO_3^- sample volume, ml

T = sampling temperature = 24.5°C

P_o = 760 mm Hg


(SS TEE)
VITON O-RING
SEALS
EXPANSION
COIL
EXHAUST
FLOW
METER
NO
VITON
TUBING
PUMP
5 LITER FLASK

a. NO DILUTION SYSTEM


NO_2
PERMEATION
TUBE
TO 5 LITER MIXING FLASK
PUMP
CONSTANT
TEMPERATURE
BATH

b. NO_2 DILUTION SYSTEM

Figure 5-1. Dilution System for NO and NO_2.

V_m = molar volume = 22.4 l/mole

f = stoichiometric factor* = 0.5 for nitrate electrode, 0.9 for PDS

V_f = sampling flask volume = 2.01 liters

T_o = 273.2°C

ΔP = final-initial pressure (of sampling vessel), mm Hg

Introducing the constants and fixed terms, this equation reduces to the formula:

$$NO_2 \text{ ppm} = 9.0 \times 10^8 \times \frac{m}{\Delta P} \quad \text{(for the nitrate electrode)}$$

$$NO_2 \text{ ppm} = 4.05 \times 10^8 \times \frac{m}{\Delta P} \quad \text{(for PDS)}$$

where m is in moles NO_3^-/l and ΔP is in mm Hg.

5.3.2.3 Stoichiometry and Analytical Methodology

Initial experiments on NO_2 absorption were run using the nitrate electrode for analysis of the nitrate formed by adsorption of NO_2. The low values for the ratio of measured to theoretical NO_2 (∿ 1:5) (Table 5-1) prompted us to investigate further. For absorption of NO_2 in caustic, the stoichiometric factor has been reported as 0.5 corresponding to the reaction:

$$2NO_2 + 2OH^- \rightarrow NO_3^- + NO_2^- + H_2O$$

The above stoichiometric factor which we measured as ∿ 0.2 (Table 5-1) assuming no oxidation of nitrite in alkaline solutions. However, Moeller (487) and Latimer (479) state that comparatively weak oxidants convert

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*Absorption of 1.0 moles of NO_2 in alkaline solution yields 0.5 moles nitrite and 0.5 moles of nitrate. The nitrate electrode does not respond to nitrite, hence a stoichiometric factor of 0.5. The PDS method does respond to nitrite (80% of nitrate) as well as nitrate. Thus, we have a factor of 0.5 for nitrate and 80% of 0.5 for nitrite or a stoichiometric factor of 0.9 for PDS.

TABLE 5-1

COMPARISON OF INITIAL (5 MIN.) NO_2 CONCENTRATIONS BY THE PDS AND NITRATE ELECTRODE ANALYSIS FOR "DRY" AIR

Run No.	NO_2 Measured (ppm)	NO_2 $\frac{\text{measured}}{\text{theoretical}}$
	Nitrate Electrode Analysis	
3	11	0.18
4	11	0.17
5	17	0.24
6	14	0.20
11	10	0.16
12	10	0.16
18	12	0.21
19	11	0.20
21	12	0.23
		0.19 - Av.
	PDS Analysis	
25	14	0.30
28	8	0.41
31	19	0.36
		0.35 - Av.

nitrite to nitrate in alkaline medium, the former citing O_2 as an example. Mellor, on the other hand, states that oxidation does not occur in neutral or alkaline solution, as implied by the Peters and Strachil technique (570).

A brief experimental investigation revealed that no oxidation occurs even with 100% (tank) oxygen for 10^{-2}M NO_2^- in .005N NaOH with reaction times as long as 16 hours. The analyses were obtained by absorption spectroscopy and are estimated as accurate at the ±1% level (since the measurements are relative not absolute).

Due to the limited sensitivity of the nitrate electrode techniques, we decided to investigate the PDS method as a readout for nitrate. Initial results using 5-minute absorption times with "dry" air revealed that the "apparent" stoichiometric factor (0.35) in Table 5-1 was nearly twice the value obtained by the nitrate electrode. Nitrite is a reported interference (547) with the PDS method but the magnitude was not given. Accordingly, we measured the effect of nitrate and nitrite mixtures by PDS analysis. The results are given in Table 5-2. These data reveal that nitrite gives 80% of the response of nitrate. The stoichiometric factors which were obtained by PDS and nitrate electrode confirm that PDS responds nearly the same to nitrate and nitrite but the nitrate electrode responds only to nitrate. Thus, the actual stoichiometric factor for NO_2 absorption in caustic becomes the ratio of nitrate electrode to PDS or 0.19/0.39* = 0.49 in good agreement with previous results (69).

TABLE 5-2

EFFECTS OF NITRITE ON THE NITRATE
ANALYSIS BY THE PDS METHOD

Sample No.	Absorbance at 400 nm	Remarks
1	0.080	25 ppm NO_3^-
2	0.130	25 ppm NO_3^- + 25 ppm NO_2^-
3	0.173	50 ppm NO_3^-
4	0.300	50 ppm NO_3^- + 50 ppm NO_2^-

5.3.2.4 Results and Discussion

The initial analytical results for NO_2 absorption were performed by nitrate electrode (as discussed in the previous section). The results for NO_2 absorption, however, have been run by the PDS technique. The low recovery of nitrate in the analysis required a study of the absorption of NO_2 as a function of time. Runs were made at 5, 30, and 60 minutes, respectively. The results are given in Table 5-3. These data showed that the absorption time for NO_2 in caustic was long ($\sim$ 1 hour) since only the values at one hour contact time were close to the NO_2 concentration added to the system. The higher (close to stoichiometric) NO_2 concentrations obtained in runs 31-33 compared to 25-27 appeared to be due to the higher relative humidity of the former runs. We proceeded to investigate the influence of moisture of the absorption of NO_2. The striking conclusion which may be drawn from runs 36-44 is that the absorption time for NO_2 in aqueous caustic becomes very rapid in moisture saturated air compared to unsaturated air of relatively high humidity. The reason for this behavior is not known, but it strongly suggests that the hydrolytic reactions discussed in Section 3 have more than academic significance. Note that the slopes rather than the absolute values in Figure 5-2 are significant. There is some scatter in the NO_2 supply level. Curve (f), for example, appears to reflect a 75 ppm NO_2 supply. Note curve (a) was run at 20 ppm NO_2 feed concentration. The data indicate that the absorption in a moist effluent will be very rapid.

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*Corrected for 80% nitrite response.

In Section 3.3, we have shown that the rate of oxidation can be predicted from Equation 12:

$$\left[\frac{1}{(P_{NO})} - \frac{1}{(P_{NO})_{In}} = k(P_{O_2})_{In}\ t\right]$$

We have run additional studies on NO using caustic absorption. The results are given in Table 5-4. Measurements were made at different contact times, O_2, and NO levels. The measured NO_2 concentrations are in good agreement with the calculated values again verifying the above equation.

If we assume a flue gas with an NO concentration of 400 ppm, and an oxygen content of 4%, for 30-second contact time the NO_2 concentration would be 12 ppm. Thus, a significant error is introduced unless the NO_2 level is high $\sim$ 1/10 the NO level. Thus, the Peters and Strachil technique (570) of two-stage absorption appears to work since

TABLE 5-3

ABSORPTION OF NO_2 IN CAUSTIC

Run No.[a]	ppm NO_2 Measured[b,c]	Absorption Time (min)	Remarks
25	15	5	(RH ∿60%) room air
26	25	30	
27	29	60	
28	8	5	(RH ∿71%) room air
29	9	30	
30	13	60	
31	19	5	(RH ∿82%) room air
32	34	30	
33	47	60	
36	81	5	Room air (saturated with water vapor at 23°C)
37	72	30	
38	72	60	
39	53	5	Room air (saturated with water vapor at 23°C)
40	53	30	
41	53	60	
42	49	5	Room air (saturated with water vapor at 23°C)
43	53	30	
44	53	60	

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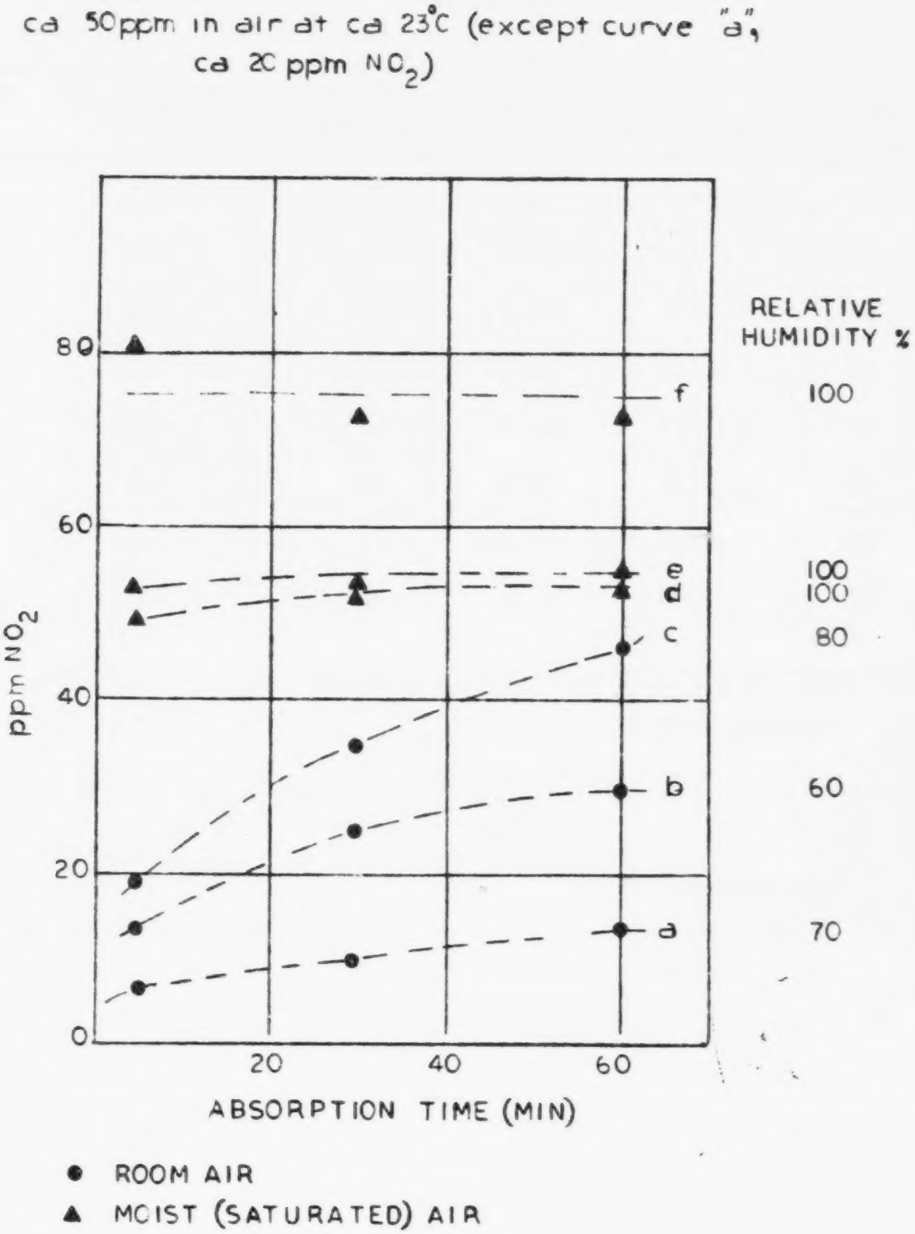
a. Two runs discarded

b. Nitrate analyses by modified PDS method

c. Nominal NO_2 concentration 50 to 60 ppm except runs 28-30 where NO_2 was ∿20 ppm.



ca 50ppm in air at ca 23°C (except curve "a", ca 20 ppm NO_2)

Figure 5-2. Effect of Moisture on the Absorption Time of NO_2 in Caustic Solution.

TABLE 5-4

COMPARISON OF CALCULATED AND MEASURED NO_2 CONCENTRATIONS FOR NO + O_2 MIXTURES

Run No.	Initial NO Conc. (ppm)	O_2(%)	Contact Time (min.)	NO_2 Measured[a] (ppm)	NO_2 Calculated[b] (ppm)
25	217	6.5	15	118	50
36	217	20.0	30	140	140
35	217	20.0	60	148	170
45	533	6.5	60	282	396
37	533	20.0	60	448	479
43	533	20.0	60	468	479
49	1009	6.5	70	752	873
47	1009	20.0	90	932	969

---

a. Nitrate analysis by nitrate electrode

b. Calculated from:

$$\frac{1}{(P_{NO})} - \frac{1}{(P_{NO})I_n} = k(P_{O_2})I_n\ t$$

(see Section 3.3)

the NO_2 is absorbed rapidly and only a small amount of NO is oxidized. However, if the NO_2 level is considerably less than 1/10 the NO concentration, the fraction of NO oxidized to NO_2 becomes a significant portion of the NO_2 measured.

5.3.2.5 Discussion and Recommendations

Additional work on actual flue gas samples is needed to confirm and evaluate the results obtained. The influence of moisture on the absorption of NO_2 should be more thoroughly investigated.

Although the chemistry of the system is complex, a two-stage caustic absorption method appears feasible for combustion effluents after further study. The NO_2 concentration should be at least 1/10 the NO concentration in order to achieve accurate results.

5.3.3 Kinetic Approach for Simultaneous Measurement of NO and NO_2

The gas phase air oxidation of NO and NO_2 is represented by the equation: $2NO + O_2 = 2NO_2$, for which the following expression relating the rate of disappearance of NO and the concentrations of O_2 and NO can be written:

$$\frac{-d[NO]}{dt} = k[O_2][NO]^2 \tag{1}$$

where [ ] denote concentrations of the various species and t = time. If O_2 is present in large excess over the NO and NO_2, $[O_2]$ can be regarded as a constant which leads to the integrated rate equation:

$$\frac{1}{[NO]} = k[O_2]\ t + \frac{1}{[NO]_o} \tag{2}$$

where $[NO]_o$ is concentration at zero time. This equation can be rewritten in terms of NO and NO_2 concentrations at:

$$\frac{1}{[NO + NO_2](1-X)} = k[O_2]\ t + \frac{1}{[NO + NO_2](1-X_o)} \tag{3}$$

where X = mole fraction of NO_2, and further simplified to:

$$\frac{1}{(1-X)} = k[O_2][NO + NO_2] + \frac{1}{(1-X_o)} \qquad (4)$$

From Equation (4), it can be seen that a plot of the reciprocal of [1-(fractional conversion of NO_2 at time "t")] versus time will give a straight line whose slope is proportional to the total [NO + NO_2] and whose intercept gives the fraction of NO_2 present in the sample at the start.

It appears technically feasible to apply the kinetic approach to the measurement of NO and NO_2 in flue gases. NO_2 would be absorbed in a suitable collecting medium and the increase of nitrate or nitrite concentration would be monitored at known time intervals after sampling. There are many possible absorbing media including water, buffered aqueous systems, oxidative solutions (such as the presently used H_2O_2/H_2SO_4 absorbers for PDS) and non-aqueous solvents. The kinetic approach was quite recently applied to the measurement of NO and NO_2 in cigarette smoke, where the NO_2 produced was measured by absorption into Saltzmann's reagent (438).

It is clear, however, that this technique would require fairly elaborate analytical facilities at the sampling site.

5.4 Conclusions

The use of solid sorbents or aqueous absorbents in the two-stage sequence discussed is a fairly simple approach to the determination of NO_2 and NO in a flue gas. The kinetic method, on the other hand, is relatively complex and not readily adaptable for field measurement. Since both the kinetic method and aqueous absorbents are best approached by grab sampling, the sensitivity for NO_2 is critical. If we estimate the NO_2 concentration as 2% of NO_x, NO_2 concentrations in power plants effluents may be expected to be in the range 5 to 20 ppm.* These concentrations are at the lower limit of sensitivity for both PDS or nitrate electrode analysis of grab samples.

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*These values are not even as low as those suggested by the thermodynamic and kinetic calculations of Section 3.

These concentrations could, on the other hand, be readily determined utilizing solid sorbents which permit longer integration times and larger sample volumes to be taken.

6. STATISTICS OF NO_x DETERMINATION

6.1 Introduction

There are major differences between the collection and analytical methods used for the oxides of sulfur and those used for the oxides of nitrogen. First, sulfur oxides are collected by techniques which concentrate the sample; nitrogen oxides are collected by grab sampling techniques. Second, many different techniques have been employed for collection and analysis of sulfur oxides in power plants (Volume I); virtually all the published and unpublished power plant analyses for NO_x have been performed by the PDS method.

Since PDS or similar techniques (grab sampling) are almost universal for NO_x, we have examined the statistics for this method in detail.

6.2 Power Plant Results

Grab sampling methods such as PDS require replicate samples (duplicate, triplicate or quadruplicate) and averaging to obtain the total NO_x concentration for a single firing condition with reasonable accuracy. We have calculated the precision of the PDS method in field sampling by computing the pooled standard deviation for a series of runs at a given power plant. For example, in Table 6-1, Test Series #1 contains nine runs in duplicate at the same power plant under different firing conditions. The results for a series of coal-fired units are summarized in Table 6-1. As expected, the precision for these analyses is considerably poorer than that reported for the determination of inorganic nitrate (analysis alone) (447). In this instance, we contend not only with the errors due to sampling and source variations, but also with the problem of the reactivity of the nitrogen oxides.

Inspection of the data in Table 6-1 reveals a correlation between the value of the mean NO_x concentration and the coefficient of variation, in the expected sense; i.e., the precision tneds to improve at higher concentrations. For comparison, we may calculate the pooled coefficient of variation for these results from the pooled variance:

TABLE 6-1

STATISTICS OF THE PDS METHOD FOR NO_x IN COAL-FIRED POWER PLANTS

Identification Number	Source	Pairs of Duplicate Samples Used	Pairs Discarded†	Mean NO_x Conc. ppm	Range (ppm)	Pooled Standard Deviation ppm	CV* %
1	548	9	0	236	150-400	32.8	13.9
2	548	14	1	387	300-460	21.0	5.6
3	442	8	1	418	220-520	17.0	4.1
4	548	10	0	424	300-560	19.0	4.7
5	548	4	1	511	400-630	41.6	8.1
6	548	15	3	964	700-1400	35.0	3.6

$$^{*}CV = \frac{\text{std. dev. x 100}}{\text{mean}}$$

†Values were discarded only where the departure from the mean exceeded 5σ, including the rejected values.

$$S^2 = \frac{\overset{i}{\Sigma} (n-1)\ S_i^2}{(\overset{i}{\Sigma}\ n_i) - i}$$

where S_i is the sample standard deviation and n_i is the statistical sample size.

For the weighted mean NO_x concentration, 527 ppm, the pooled coefficient of variation is calculated to be 5.3%.

An additional datum has been provided by D. Barnhart (425) who summarized PDS precision in coal-fired power plant sampling as ±25 ppm at 250 ppm NO_x.

Since these data on the precision of the PDS method in coal-fired power plants shows some degradation at NO_x concentrations less than 400 ppm, we have investigated the possible importance of fuel type by searching for additional NO_x field data from various sources.

Measurements of NO_x concentrations at a number of gas-fired plants were obtained from Combustion Engineering (442), Foster Wheeler (560), Riley Stoker (561), and Bary Area APCD (562). Another series of measurements at a gas-fired power plant was obtained from NAPCA (548). The results are summarized in Table 6-2. The precision of these results is in the same range as those of the coal-fired power plants; the trend toward decreased precision at low NO_x concentrations is apparent in both data sets.

There are several differences, however, between the data in Tables 6-1 and 6-2. The measurements at the gas-fired power plants were obtained from five different laboratories but the coal-fired power plant data are essentially from one laboratory (NAPCA). Thus, the gas-fired data may be expected to have a greater variance due to differences in techniques between laboratories. The important thing to note is that the trend in the data for an individual laboratory is consistent (i.e., precision decreases with concentration).

TABLE 6-2

STATISTICS OF THE PDS METHOD FOR NO_x IN GAS-FIRED POWER PLANTS

Identification Number	Source	Number of Samples Used	Number Discarded	Mean NO_x Conc. ppm	Range (ppm)	Pooled Standard Deviation (ppm)	CV %
1	562	7 D		99	10-150	12.9	13.1
2	561*	12 D		114	70-150	9.0	7.9
3	442	7 D		152	90-220	13.8	9.1
4	548	12 D		286	260-315	12.1	4.2
5	442	6 T		294	230-250	14.9	5.1
6	562	4 D		331	210-450	25.0	7.6
7	560*	6 D	1	433	300-600	38.1	8.8
8	561*	4 Q		443	320-500	29.8	6.8
9	560*	8 T	1	545	310-680	38.1	7.0
10	442	8 T		589	320-720	27.8	4.8

---

*Data not included in Figure 6-1

D = duplicate samples

T = triplicate samples

Q = quadruplicate samples

Some additional results for oil-fired power plants (563,561) are given in Table 6-3.

To determine the variation of the precision with NO_x concentration, we have combined the data of Tables 6-1 to 6-3 and conducted logarithmic regression analysis of the pooled data (weighted for sample size) to obtain best estimates of the coefficient of variation as a function of NO_x concentration (Figure 6-1). The pooled estimate of the coefficient of variation is 3% at 1000 ppm and 10% at 100 ppm NO_x.

6.3 PDS Automotive or Diesel Exhaust Results

Data on the analysis of NO_x in auto exhaust (26 tests) were obtained from B. Dimitriades of the Bureau of Mines (564). Grab samples were taken in quadruplicate from a mylar bag in which the exhaust was collected (7). This method should eliminate source variation from calculated precision values. We have divided the data into three concentration ranges and have calculated the precision statistics given in Table 6-4. This technique yields precision values comparable to the precision of the analytical method alone, i.e., sampling errors are essentially eliminated. Additional data were obtained from H. Lang at the Bureau of Mines (20 sets) for NO_x in diesel exhausts by the PDS method (565,566). These samples were taken "on stream" and, therefore, include sampling errors. The coefficient of variation for these samples is, as expected, somewhat higher than Dimitriades' results (2.5 compared to 1.8%).

The precision for 21 individual diesel exhaust samples obtained under standard test conditions by David and O'Neil (9) over an extended period of time is C.V. = 6.9% at mean NO_x = 636 ppm. The influence of source variation on the precision of NO_x sampling is readily seen by comparison to the precision obtained by Lang for duplicate samples.

6.4 Comparison of the Precision of PDS to the Precision of Other Methods for NO_x Determination

The PDS method has been used almost exclusively in power plants. The British Standards Institution recommends the 2,4-xylenol method which

TABLE 6-3

STATISTICS OF THE PDS METHOD FOR NO_x IN OIL-FIRED POWER PLANTS

Identification Number	Source	Number of Samples Used	Number Discarded	Mean NO_x Conc. ppm	Range (ppm)	Pooled Standard Deviation (ppm)	CV %
1	561*	4 D		167	110-240	22.7	13.6
2	561*	10 D		221	160-265	8.5	3.9
3	561*	4 Q		320	230-390	51.5	16.0
4	563	18 D	2	445	340-520	30.2	6.8
5	563	11 D	6	672	560-690	34.2	5.1

---

*Data not included in Figure 6-1

D = duplicate samples

Q = quadruplicate samples

Figure 6-1

Precision of NO_x Determination by PDS Method in Fossil Fuel Fired Power Plants

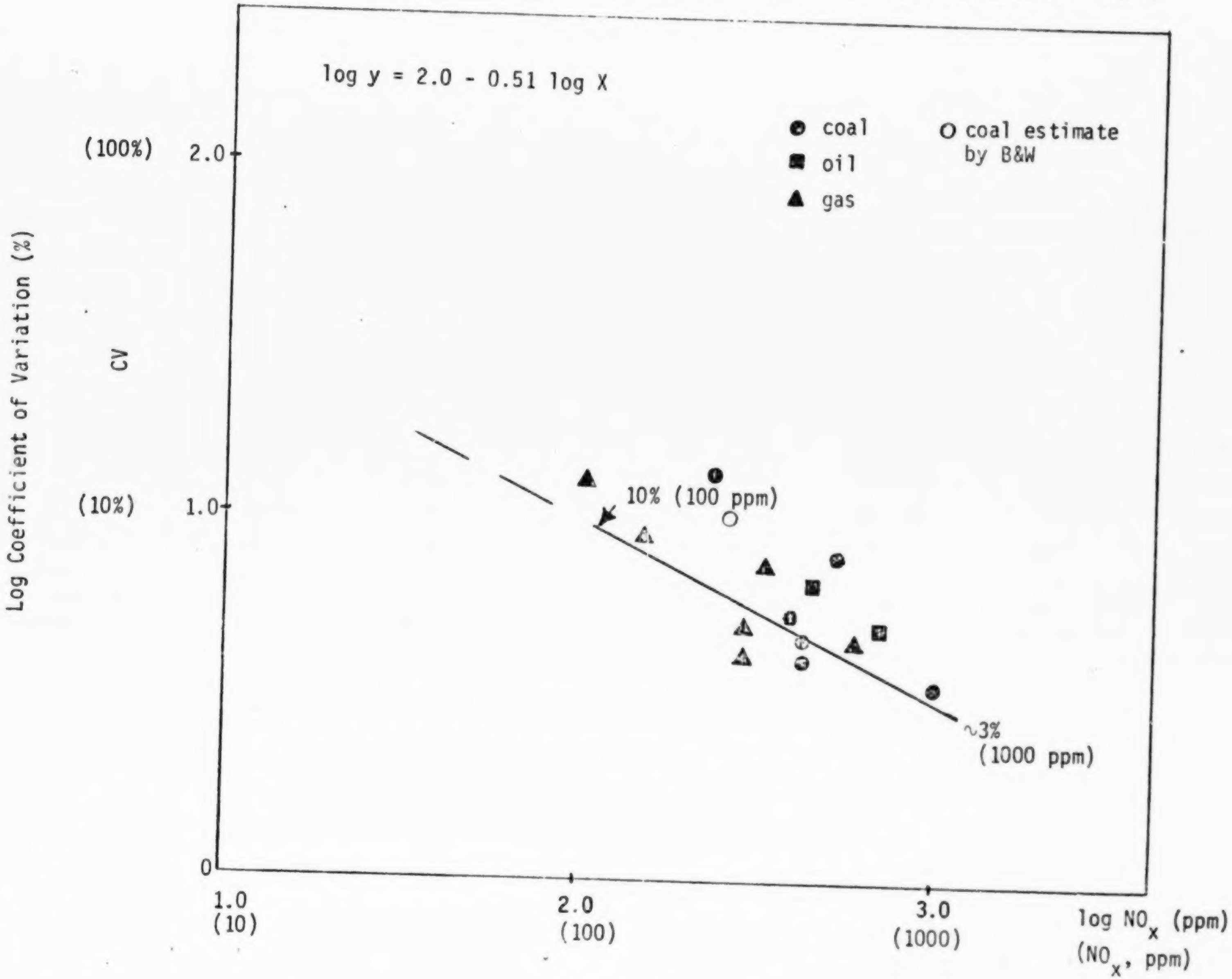

TABLE 6-4

PDS STATISTICS FOR AUTOMOTIVE EXHAUSTS

No. of Samples	Mean NO_x Conc. (ppm)	Range	Standard Deviation (ppm)	CV %
13*	169	37-237	4.8	2.9
8*	449	347-526	4.6	1.03
5*	633	633-690	11.4	1.8
10†	667	445-855	16.8	2.5
10†	1003	890-1200	13.0	1.3

---

*Run in quadruplicate (564)

†Run in duplicate (566)

also utilizes evacuated flask sampling and colorimetric readout. It is not surprising, therefore, that the precision of the determination, reported to be ±5% (379), is similar to that found for the PDS method.

In a series of tests on diesel exhaust gases, the PDS and modified Saltzmann methods were run in duplicate and compared to mass spectrometric results (565). The results of the individual duplicate wet chemical samples were obtained from H. Lang (566). The precision of these results is given in Table 6-5, series #1 and 2. The PDS method gives slightly better precision than the modified Saltzmann method. Results from comparison of PDS and modified Saltzmann methods, also for diesel exhausts, taken from (9) are given in Table 6-5, series #3-10.

In order to compare these two sets of data, we calculate the pooled coefficient of variation for all the data in Table 6-5. The results are given below:

TABLE 6-5

COMPARISON OF THE PRECISION OF THE PDS AND SALTZMANN METHODS FOR NO_x IN DIESEL EXHAUSTS

Series No.	Source	Number of Tests	Mean NO_x Conc. ppm	Pooled Standard Deviation ppm	CV %	Method
1	566	20[†]	835	15.0	1.8	PDS
2	566	20[†]	846	29.1	3.5	Saltzmann
3	9	21	636	44.0	6.9	PDS
4	9	21	678	27.0	2.5	Saltzmann
5	9	5	937	29.0	3.1	PDS
6	9	5	915	20.0	2.2	Saltzmann
7	9	4	1096	18.0	1.7	PDS
8	9	4	1118	15.0	1.3	Saltzmann
9	9	2	1811	42.0	2.3	PDS
10	9	2	1817	18.0	1.0	Saltzmann

[†] Duplicate samples

Method	Mean NO_x Conc. (ppm)	Pooled Coefficient of Variation (%)
PDS	825	3.4
Modified Saltzmann	842	3.2

Thus, we find that the precision of the Saltzmann is essentially the same as for the PDS method. As above, both methods which again use similar techniques (evacuated flasks) and colorimetric readout yield the same precision for diesel exhaust.

Lang, et al. (565) compared both the PDS and the modified Saltzmann methods to nitric oxide determination by the mass spectrometer. If we assume that the mass spectrometer results are accurate,* we can compute the accuracy of these wet chemical methods using the simple linear regression method.

Taking the mass spectrometer as the dependent variable and the PDS as the independent variable, the regression equation for the 20 set population is:

$$Yms = -7.4 + 1.0\ X_{PDS}$$

$$\text{mean } (\bar{S}) = 840 \text{ ppm}$$

$$(SE) = 45 \text{ ppm}$$

$$(CV) = 5.4\%$$

$$(CD) = 0.96^{\dagger}$$

For the Saltzmann method as the independent variable and the mass spectrometer as the dependent variable, the regression equation for the 20

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[*] This should be a valid assumption since the major oxide component is nitric oxide, and the sample is introduced directly into the inlet system where the pressure is immediately reduced, minimizing the possibility of oxidation.

[†] CD = coefficient of determination - the square of the correlation coefficient which may be interpreted so the fraction of the total sample variance accounted for by the regression equation.

set population is:

$$Yms = -43.4 + 1.0\ X_{SA}$$

$$\text{mean } (\overline{S}) = 840 \text{ ppm}$$

$$(SE) = 48 \text{ ppm}$$

$$(CV) = 5.7\%$$

$$(CD) = 0.96$$

The unit slope, small intercept, and high coefficient of determination for both wet chemical methods indicates that interferences in NO_x determinations in diesel exhaust are minimal at these concentrations.

6.5 Conclusions

The coefficient of variation for the NO_x measurements in power plants by the PDS method is dependent on the concentration (CV = 10% at 100; 3% at 1000 ppm NO_x).

No apparent differences have been found for variations in fuels but we intend to examine this effect in more detail by obtaining data on the three major fuels run by the same laboratory.

Accuracy of the order of 5 to 6% is found for diesel exhausts, however, the accuracy may be poorer for power plants where more severe sampling problems are encountered.

The precision of the PDS method for NO_x (in diesel exhausts) is about the same as that for the similar Saltzmann and 2,4-xylenol methods.

7. RECOMMENDATIONS

7.1 NO_x Determinations

The phenol disulfonic acid method has been found to be a reliable and the most generally applicable method for total oxides of nitrogen in combustion effluents. The rate controlling step for the sampling procedure is the gas phase oxidation of NO to NO_2. The colorimetric analysis is also slow as a result of the long (2 to 6 hour) evaporation time required.

The PDS procedure may be substantially improved by (successful) development of:

(1) Addition of oxygen or ozone to the sampling vessel to reduce absorption time.

(2) Use of rotary (or other) fast evaporation equipment and smaller aliquots for the present colorimetric determination of nitrate.

(3) Direct determination of nitrate in the absorber solution with the specific ion electrode.

(4) Nitration in 50% sulfuric acid (instead of evaporation to dryness). See Section 4.3.1.

An alternative approach of great promise is the use of reactive solid sorbents. If successfully developed, solid sorbents may yield considerably higher precision and accuracy than presently attainable, greater east of use, and possibly permit simultaneous SO_x and NO_x determination. The nitrate electrode yields a rapid analysis for nitrate and gave good agreement with PDS for the limited samples taken. This technique should be validated as a replacement for the time-consuming PDS technique.

7.2 NO/NO_2 Determinations

The most promising approach to NO/NO_2 analysis is development of new sampling techniques to be used with existing nitrite and nitrate methods. The sampling methods include solid sorbents and/or aqueous absorbents used in two-stage sequence. The two-stage caustic absorption technique appears to be feasible for NO_2/NO_x ratios of 1:10. Kinetic analysis may be a feasible alternative if simple analytical determinations are developed.

7.3 Simplified Methods

The modified Saltzmann method or hydrogen peroxide collection followed by NaOH titration are simplified methods which may be used for total NO_x determinations in a gas-fired power plant, i.e., in an effluent free of SO_2. Ferrous sulfate and other complexes may be considered as candidate simplified methods for total NO_x determinations. Solid sorbents because of their ease of use may also be considered as simplified methods. The nitrate electrode promises to be a simplified method with nearly the same precision as the PDS method.

8. CONCLUSIONS

Thermochemical and kinetic data reveal that N_2O_4, N_2O_5, and NO_3 do not exist in significant concentrations in flue gases. At equilibrium, significant concentrations of N_2O and $HNO_3(g)$ may exist in a flue gas at low temperatures. NO and NO_2 are the major oxides emitted in combustion processes. Analysis of the (homogeneous) kinetics shows that for typical flue gas conditions and 600 ppm NO, the NO_2 concentration is only 1 ppm (assuming no SO_2 in the flue gas) for typical residence times. There appears to be no experimental basis for the high NO_2/NO_x ratios (10%) commonly reported for flue gases. No reliable measurements of NO_2 in power plant effluents have been located.

All sampling procedures for NO_x determination in stack gases require grab sampling techniques because of the low solubility of NO in aqueous solutions. Integrated grab sampling should provide improved results in emissions determinations.

A large number of analytical methods for both nitrate and nitrite have been evaluated. Many of these methods have drawbacks such as limited range, interferences, many procedural steps, etc. The methods which determine nitrite present a problem because SO_2, which is present in high concentrations in oil- and coal-fired plants, will reduce nitrite in acid solutions. The PDS method (for nitrate) is the only one which has been widely used for the determination of NO_x in power plants. The major drawback to this technique is the long time required for analysis. Two steps in this procedure are time consuming:

(1) oxidation of NO to NO_2
(2) evaporation of absorbing solution

The time required to carry out the oxidation may be reduced by an order of magnitude or more by O_2 or O_3 enrichment. The evaporation time may be reduced by use of a rotary evaporator in place of a steam bath or by nitration in 50% H_2SO_4 (620).

The nitrate electrode has been tested for NO_x determination. Preliminary results at oil-fired power plants show good agreement (within ±5%) with PDS. This method has the advantage of rapid readout of the nitrate concentrations.

Solid sorbents are promising candidates for development of methods for total NO_x as well as NO/NO_2, which are both convenient and of high precision. Two-stage absorption in aqueous NaOH appears to be a feasible method for the determination of NO_2 in combustion effluents provided that the NO_2/NO_x ratio is about 1:10.

The coefficient of variation for NO_x determination in power plants by the PDS method is dependent on the concentration (CV = 10% at 100; 3% at 1000 ppm NO_x). No apparent differences in precision have been found as a function of fuel, although we are seeking analytical data for the three major fuels conducted by the same laboratory.

Accuracy of the order of 5 to 6% is found for diesel exhausts; however, the accuracy may be poorer for power plants where more severe sampling problems are encountered.

The precision of the PDS method for NO_x (in diesel exhausts) is about the same as that for the similar Saltzmann and 2,4-xylenol methods.

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APPENDIX 1

LITERATURE SEARCH

A comprehensive search of the literature was conducted to learn of all methodology which might be applicable to this program. This includes methods currently in use, those used in the past which seemed appropriate, and information from other areas which seemed relevant.

In order to perform this study, we made a thorough search of the literature both past and present. Thus, we covered journals, abstracts, indices, and bibliographies shown in Tables A1-1 and A1-2. By this approach, we feel we covered all journals in the western world and many others which might have any pertinence to this problem. To supplement this, we requested and obtained a literature search by APTIC on sampling and analytical methods for the pollutants of interest.

As articles of interest were uncovered by the literature research staff, the papers were studied by analytical chemists and significant information abstracted for further evaluation. As the study progressed, group discussions were held with chemists with relevant experience in order to both evaluate existing methods and seek fresh alternatives.

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TABLE A1-1

PRIMARY LITERATURE SOURCES UTILIZED IN THIS PROGRAM

Air Pollution Control Abstracts	1956-1969
Air Pollution Titles	Thru 1969
American Petroleum Institute Proceedings	1962-1969
Analytical Abstracts	1954-1969
Applied Science and Technology Index	1939-1969
Chemical Abstracts	1907-1968
Chemical Titles	Thru 1969
Engineering Index	1939-1969
Fuel Abstracts and Current Titles	1960-1969
SAE Progress in Technology Series	1961-1967

TABLE A1-2

BIBLIOGRAPHIES

Air Pollution Publications: A Selected Bibliography (DHEW)	1963-1966
DDC Bibliography on Air and Water Pollution (1968) AD 679210	
Research into Sampling, Analysis and Monitoring of Gaseous Pollutant Emissions from Stacks Literature Searches I and II (Engineering Found)	1963,1965
Sulfur Oxides and Other Sulfur Compounds A. G. Cooper, DHEW	1965

APPENDIX 2

SAMPLING SYSTEM FOR SO_x AND NO_x

Equipment for sampling SO_x (and NO_x) gases from combustion flue gases has been designed. The objectives of the design were first to provide high precision and secondly, to make the equipment convenient to transport, install, and operate at field locations. The system is comprised of the following three modules:

1. dual probe module
2. SO_x and NO_x collection module
3. control module

The above modules constitute a complete system for sampling for SO_3, SO_2, and NO_x in the flue gas.

Probe Module - A schematic of the probe module is shown in Figure A2-1. The features of this module are:

1. Dual probes, a 1/4-inch diameter stainless steel probe for NO_x mechanically coupled to 11 mm pyrex probe for SO_x.

2. Pyrex probe electrically heated to prevent condensation of SO_3 in the sampling line.

3. Stack adapter assembly that allows various probe insertion depths.

4. Filter in the probe to remove particulates from the SO_x sample gas.

5. Quick attachment tees for NO_x grab samplers.

6. Pyrex socket joint for connection to collector module.

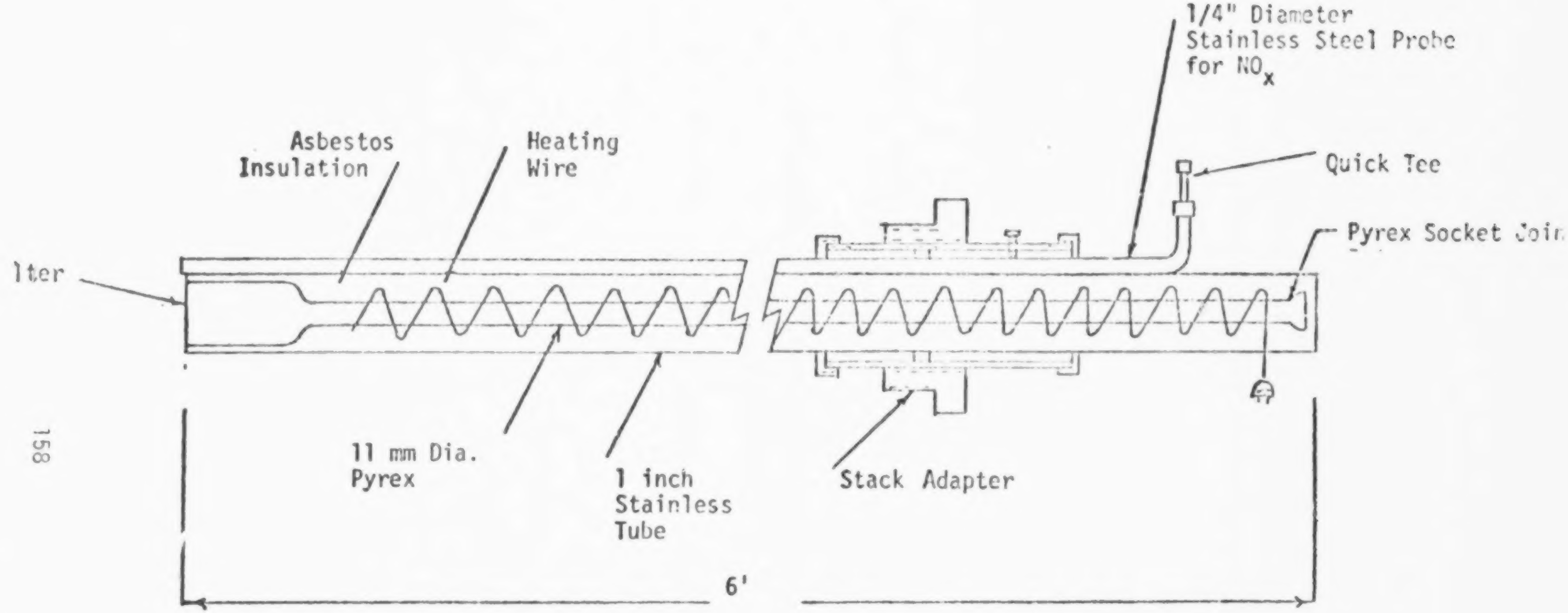
1/4" Diameter
Stainless Steel Probe
for NO_x
Asbestos
Insulation
Heating
Wire
Quick Tee
Pyrex Socket Joi
lter
11 mm Dia.
Pyrex
1 inch
Stainless
Tube
Stack Adapter
6'

Figure A2-1. Probe Module.

APPENDIX 3

SIMULTANEOUS EQUILIBRIUM PROGRAM DESCRIPTION - DEQL

The program DEQL was designed to carry out the equilibrium calculation for a series of chemical reactions occurring simultaneously. The calculation follows an iterative procedure, examining each reaction separately and, in each case, bringing the concentrations of the reactants to equilibrium. When the change in reactant concentrations on successive iteration steps becomes less than some preset margin of precision, the iteration is stopped and the final reactant concentrations are printed out. Experience with this program has shown that convergence is quite rapid. In one case with eight reactions and with a margin of precision of .1%, only four iteration cycles (each cycle calculates equilibrium for all eight reactions) were required for convergence on a solution.

In its present form, the program allows up to eight reactions with six reactants to be included. As input it requires the reaction temperatures, the reaction equilibrium constants, and the initial concentrations of the reactants. The program output gives the equilibrium concentrations of the reactants.

DEQL has been written in FORTRAN IV and has been used at Walden on a time shared IBM 360/67 computer. Running times for the program have been about four seconds, CPU time (including program loading and execution) for a calculation involving eight reactions and about four iteration cycles.

APPENDIX 4

LABORATORY STUDIES OF THE CHROMATROPIC ACID METHOD FOR NITRATE

We have investigated the use of chromatropic acid (2,7-dihydroxy-naphthalene-4,5-disulfonic acid; abbreviated "CA") (10) for analysis of nitrogen oxides because of its apparent high selectivity for nitrate and ease of application. CA is made up as an 0.01% solution in concentrated H_2SO_4, and 7 ml of this solution are mixed with 3 ml of aqueous sample. The reaction mixture is allowed to cool to room temperature, and the yellow color resulting from nitration of the CA is measured spectrophotometrically. The CA reagent in 70% H_2SO_4 has absorption maxima at 234 nm, 310-316 nm (broad), 332 nm and 346-348 nm. Reaction of the CA reagent with aqueous samples containing 5-15 ppm nitrate, resulted in decreases in all the reagent peaks (above) and the appearance of two new ones at 357 nm (appearing as a shoulder on the 347 nm reagent peak) and at 420 nm. When high concentrations (300-1000 ppm) of nitrate were used, the absorbance in the 420 nm region did not obey Beer's law but decreased with increasing amounts of nitrate.

The CA reagent also reacts with formaldehyde (CA is a well-known colorimetric reagent for formaldehyde) to give a purple color, which absorbs slightly in the 420 nm region, A_{420} for a 30 ppm CH_2O sample is equivalent to that from a 3 ppm of nitrate. Thus, the formaldehyde interference is not very important. Since the CA gives a yellow-brown color even with traces of oxidants, excess oxidant must be removed before resetting the sample with the CA reagent. We used a 30 ppm solution of formaldehyde in water as the standard, although this represented a larger amount than would be expected. We tested as oxidants 1% H_2O_2, 0.1 M $KMnO_4$ and 0.3 M $K_2S_2O_8$. Up to 2 ml of H_2O_2 were allowed to react with 10 ml of 30 ppm CH_2O for up to one hour with no observable effect on the CH_2O-CA color. The product of the reduction of $KMnO_4$ with Na_2SO_3 was MnO_2, which oxidized the CA reagent in the 70% H_2SO_4 color development solution. The $K_2S_2O_8$ (approximately 0.3 M close to saturation) did

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remove the formaldehyde after standing overnight, but not after only six hours of standing. Our experiments indicate that removal of CH_2O at these low levels will be very difficult to accomplish.

Since CA is extremely sensitive to oxidants (such as H_2O_2) normally present in the acidic absorption solution used for sampling nitrogen oxides, it would have to be removed by addition of a reagent such as Na_2SO_3 or boiling to decompose the peroxide. Another problem with CA is that the reaction with nitrate produces a very broad absorption band in the 400-450 nm region which may suffer from interferences due to unburned hydrocarbons.

Because of the lack of a unique absorption spectrum, the possible interferences from traces of unburned fuel and CH_2O and sensitivity to oxidants, chromatropic acid offers no advantages over the phenol disulfonic acid reagent. Investigation of this reagent for an improved method was, therefore, abandoned.